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Paul B. Langford IV

A STUDY OF SOME CARBANIONS DERIVED FROM ORGANIC HALOGEN COMPOUNDS

Part I

THE REACTION OF beta-HALOETHYL BROMIDES WITH SODIUM HYDROXIDE

Part II

THE BASE CATALYSED DEHYDROHALOGENATION OF beta-BENZENE HEXACHLORIDE

A THESIS

Presented to

the Faculty of the Graduate Division

by

Paul Brooks Langford

In Partial Fulfillment

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Doctor of Philosophy in the School

of Chemistry

Georgia Institute of Technology

June, 1962

A STUDY OF SOME CARBANIONS DERIVED FROM ORGANIC HALOGEN COMPOUNDS

Part I

The Reaction of beta-Haloethyl Bromides

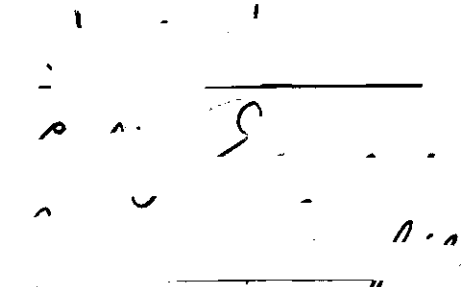
with Sodium Hydroxide

Part II

The Base Catalysed Dehydrohalogenation

of beta-Benzene Hexachloride

APPROVED:



Date Approved by Chairman: June 2, 1962

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Part II

Part I

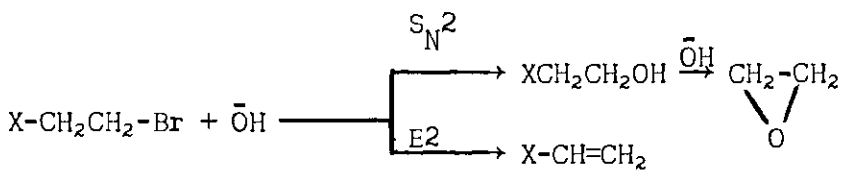
THE REACTION OF beta-HALOETHYL BROMIDES WITH SODIUM HYDROXIDE

SUMMARY

Part I

Information concerning the effect of a beta-halogen substituent on the E2 reactivity of another halogen has been obtained from product studies and kinetic studies. These substituents have been shown to increase the E2 reactivity when either bromine or chlorine is in the beta-position in either open chain or cyclic dihalides. Up to this time, none of the previous studies have included fluorine or iodine substituents. Earlier workers concluded that all beta-halogens increase E2 reactivity and that this affect is primarily due to the inductive effect of the beta-halogen which makes the beta-hydrogen more acidic. It is possible to make a direct comparison of the relative extents to which beta-halogen substituents effect E2 reactivity by investigating the reactions of beta-fluoroethyl bromide, beta-chloroethyl bromide, and beta-bromoethyl bromide with sodium hydroxide. beta-Iodoethyl bromide was not studied because the iodo substituent is removed by nucleophilic attack at a rate comparable to that of beta-hydrogen removal.

The reactions between beta-haloethyl bromides and sodium hydroxide may follow either of two possible paths, substitution, S_N2, or elimination, E2.



By using hydroxide ions it is possible to determine the extent to which the reaction has followed each of the two paths. This is because the substitution product, an ethylene halohydrin, is much more reactive toward hydroxide than the starting halide but the elimination product, a vinyl halide, is much less reactive.

The data obtained in the present studies are summarized in Table 1. The beta-substituent halogens are seen to affect the E2 reactivity of the compounds in the order

$$Br > Cl >> F$$

with both bromine and chlorine being much more effective than fluorine. This is the opposite of what would be expected by considering the inductive effect only.

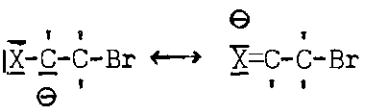
The data seem explicable on the basis of two factors, acidity of the beta-hydrogen and stability of the olefin being formed.

The ability of halogens to increase the acidity of the beta-hydrogen in the order

$$Br > Cl >> F$$

may be explained by a consideration of the following factors:

(1) d-Orbital Resonance. Stabilization of the carbanion is possible by resonance structures of the type



having 10 electrons in the outer shell of the halogen atom. The high energy necessary to expand the octet of fluorine may explain why fluorine is the poorest of the three halogens studied at facilitating removal of

the beta-hydrogen by base even though it has the greatest electronegativity. Divalent sulfur is reported by other workers to be better than divalent oxygen at facilitating beta-hydrogen removal by base.

(2) Polarizability. With respect to polarizability, the order of the halogens is

$$Br > Cl >> F$$

with fluorine being much less polarizable than either of the other two halogens.

Both of these effects, (1) and (2), would give the activation order

$$Br > Cl >> F$$

which is the same as the order determined experimentally in the present work.

Unlike chlorine and bromine, fluorine substituents appear to destabilize olefins relative to the corresponding saturated compounds.

It seems then that all these results can be explained by assuming that changes in both the beta-hydrogen acidity and the stability of the olefin being formed are important factors.

Table 1. Kinetic Constants for Reaction with Sodium Hydroxide in 50% Aqueous Dioxane.

Compound		10^4k (l./moles-sec.) 30.0°	70.0°	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
$BrCH_2CH_2Br$[a]	E2	3.17 ± 0.17	180 ± 10	20.2 ± 0.5	-7.8 ± 1.7
	S_N2	0.17 ± 0.17	10 ± 10	- - - - - -	- - - - -
$ClCH_2CH_2Br$	E2	2.21 ± 0.06	122 ± 4	20.1 ± 0.3	-9.9 ± 1.0
	S_N2	0.06 ± 0.06	4 ± 4	- - - - - -	- - - - -
FCH_2CH_2Br	E2	0.050 ± 0.050[b]	0.94 ± 0.30	- - - - - -	- - - - -
	S_N2	0.495 ± 0.050[b]	3.52 ± 0.35	21.1 ± 2.0	-13.2 ± 6.0
CH_2=CHBr		0.0014 ± 0.0004	0.27 ± 0.05[c]	23.9 ± 3.0	-11.1 ± 10.0

[a] The rate constants have been divided by a statistical factor of two to give the rate constant per bromine.

[b] At 50.1°C. [c] At 75 ± 2°C.

CHAPTER I

INTRODUCTION

Several studies have shown that both beta-chlorine and beta-bromine substituents increase the rate of E2[1] (alkaline dehydrohalogenation) reactions (2,3,4). These data have led to the generalization that the influence of beta-halogen substituents is due primarily to the inductive effect, which makes the beta-hydrogen atoms more acidic (1). Goering and Espy (4) made a comparison of beta-bromine and beta-chlorine substituents on E2 reactivity in some dihalocyclohexanes. They found that both beta-bromo and beta-chloro substituents increase E2 reactivity, the beta-bromo substituent having a slightly greater effect than the beta-chloro substituent. However, there did not appear to be any direct comparison of the relative extent to which beta-substituent halogens, including fluorine, affect E2 reactivity. Such information has been obtained by studying the reactions between beta-fluoroethyl, beta-chloroethyl, and beta-bromoethyl bromides and sodium hydroxide in 50 volume per cent aqueous dioxane. These compounds were studied because of their simplicity which reduces the complications sometimes encountered in more complex molecules. The fluorine compound was included because

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[1] For a thorough discussion of the terms E2 and S_N2 see reference (1).

1. C. K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, New York, 1953, Chapters VII and VIII.
2. S. C. J. Oliver and A. P. Weber, Rec. trav. chim., 53, 1087 (1934).
3. S. C. J. Oliver, ibid., p. 1093.
4. H. L. Goering and H. H. Espy, J. Am. Chem. Soc., 78, 1454 (1956).
5. C. K. Ingold, op. cit., p. 446-7.

apparently the effect of beta-fluorine substituents had not been investigated previously. beta-Iodoethyl bromide was not studied because beta-iodo substituents have been found to be removed at a rate comparable to beta-hydrogen removal (6). By using hydroxide ions, the relative extent to which the reaction follows the elimination path and the substitution path could be determined. It was thus possible to obtain rate constants for both the E2 and S_N2 reactions of these compounds with hydroxide ions and also values for the heats and entropies of activation.

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6. J. Hine and W. H. Brader, Jr., J. Am. Chem. Soc., 75, 3964 (1953).

CHAPTER II

PROCEDURE

Experimental

Kinetics of the beta-Haloethyl Bromide + Sodium Hydroxide Reactions.--All three of the dihalides studied were run in the same manner. Standardized, carbonate-free, aqueous sodium hydroxide solutions were mixed with purified dioxane and a small volume of diphenylamine in dioxane solution such that the final concentration of diphenylamine was 0.001 M. The amine was added to prevent the free radical polymerization of the vinyl halide product. In runs where this was not added, the rate constants tended to increase, presumably due to the dehydrohalogenation of polyvinyl halide. To this thermostated mixture was added a thermostated solution of the halide in dioxane (a stock solution was prepared by weighing the halide and dissolving in dioxane). The flask was shaken and replaced in a bath in which the temperature was controlled to $\pm$ 0.05°C[1]. Total volumes used were near, but not exactly, 500 ml. since there is some shrinkage in mixing aqueous and dioxane solutions. This was taken into account when the rate constants were calculated. For the reactions at 30°C, from time to time 50 ml. aliquots were pipetted into a flask and immediately titrated with hydrochloric acid solution to the phenolphthalein end point. Since the reactions at 30°C were relatively slow, the reaction taking place during the transfer was

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[1]The bath has been described by J. Hine and W. H. Brader (6).

negligible. In the beta-chloroethyl bromide and beta-bromoethyl bromide runs at 70°C[1], however, the 50 ml. aliquot was added to excess hydrochloric acid solution and back titrated since these reactions were relatively fast.

Reaction times reported in hours were measured using an electric clock with second hand. Those reported in minutes and seconds were measured with a stop watch or electric timer, both marked in units of one-tenth second.

Determination of the Volume Contraction in Forming Water-Dioxane Solutions.--The extent of shrinkage was determined by mixing 25.00 ml. of aqueous 0.0542 N sodium hydroxide solution with 25.00 ml. of pure dioxane. Two separate determinations gave 48.95 and 48.90 ml. respectively for the total volume. Enough 50 volume per cent aqueous sodium hydroxide-dioxane solution had previously been added to fill the buret up to the 50.00 ml. mark. After inverting the buret several times and allowing the solution to cool to room temperature, the volume reading on the buret was substracted from 50.00 ml. to obtain the volume of the mixture. Since the solutions for kinetic runs were made up by mixing 250 ml. of about 0.05 N aqueous sodium hydroxide with 250 ml. of about 0.01 M halide in dioxane solution, the actual concentrations of halide and base in the solution were calculated by multiplying the known concentration of the base or halide in the 250 ml. of solution before mixing by 0.50 x 50.00/48.93.

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[1] A light mineral oil was used in place of water in the constant temperature bath previously described to prevent temperature fluctuations due to evaporation.

Determination of f for beta-Haloethyl Bromide and Sodium Hydroxide.--The term f is defined as the fraction of the reaction taking place by substitution. Using the f values determined experimentally (by allowing the reactions to go to completion and determining the total quantity of base used up) in calculating rate constants invariably gave decreasing constants. This was probably due to the slow reaction of the vinyl halide product. Several attempts to check the determination of f were not successful. Analysis of ethylene oxide produced in the reaction was not possible because the oxide was hydrolysed to the glycol at a rate comparable to the reaction rates being studied (7). Hydration of ethylene oxide to ethylene glycol and titration of the glycol with periodic acid (8) was not successful due to interference by bromide ion. The f value used in the calculations was calculated by taking one point at 90-92 per cent completion (but early enough so that no appreciable reaction of vinyl halide had occurred) and choosing, by successive approximation, the value of f which gave a value of k_2 (the second order rate constant for reaction between base and halide) for this point equal to the average of the values calculated from the earlier points.

Kinetics of the Vinyl Bromide + Sodium Hydroxide Reaction.--This reaction at 30°C was carried out by mixing thermostated solutions of carbonate-free aqueous sodium hydroxide, vinyl bromide in dioxane (containing a small amount of diphenylamine to prevent polymerization), and sufficient

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7. H. J. Lichtenstein and G. H. Twigg, Trans. Faraday Soc., 44, 905 (1948).

8. J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer, and A. Weissberger, Editors, Organic Analysis, Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953, p. 41-47 and 147-9.

pure dioxane to make approximately 500 ml. of 50 volume per cent aqueous dioxane solution. Fifty ml. aliquots were pipetted out and titrated with standard HCl solution to the phenolphthalein end point. The reaction at 75°C was run in exactly the same manner but the temperature was not controlled very accurately (±2°C) since it was desired to obtain an approximate rate constant to compare to those of the dihalides.

Times were measured using an electric clock with second hand.

Preparation and Purification of Reagents

beta-Fluoroethyl Bromide.--This compound was prepared according to the method of Hoffman (9). About 600 ml. of dry ethylene glycol was placed in a one liter flask fitted with dropping funnel, side arm, and thermometer. A water-cooled condenser with 250 ml. receiver was attached. Two moles (116 g.) of anhydrous potassium fluoride[1] was added to the glycol and the mixture was heated to 170°C to dissolve the salt. After the mixture had been cooled to 150°C, 300 g. of ethylene bromide was added over a period of five hours. The ethylene fluorobromide was removed by distillation and while the reaction flask was still at 150°C, 75 g. more (total of 2 moles) of ethylene bromide was added slowly, following which the mixture was heated to distill the fluorobromide. The dihalide distillate was drawn off from the glycol-water layer and purified by distilling twice through a 16 x 1/2 inch Stedman type column. The

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9. F. W. Hoffman, J. Am. Chem. Soc., 70, 2596 (1948).

[1]Prepared by heating $KF \cdot 2H_2O$ (Baker and Adamson, purified) at 130°C for three days in a vacuum oven.

final product, weighing 12.3 g., boiled at 69-70°C at 742 mm. and had a refractive index of 1.4218 at 25°C. These physical properties compare favorably with those reported by Henne and Renoll (10); b.p., 71.5-71.8°C at 760 mm. and n_D^{25}, 1.42261.

beta-Chloroethyl Bromide.--This compound was a commercial product and was distilled through the Stedman column. The observed physical constants were: b.p., 107-8°C at 733 mm., uncorrected; n_D^{28}, 1.4863. The physical constants reported in the literature (11) are: b.p., 106.7°C; n_D^{20}, 1.49174.

beta-Bromoethyl Bromide.--This compound (ethylene bromide) was a commercial product and was distilled through the Stedman column. The observed physical constants were: b.p., 127.5-128.0°C at 739 mm., uncorrected; n_D^{28}, 1.5345. These compare favorably with those reported in the literature (12) which are: b.p., 131.5-131.7°C at 760 mm.; n_D^{25}, 1.5355.

Vinyl Bromide (13).--An excess of redistilled, commercial ethylene bromide was added to a flask to which was attached a reflux condenser and in which was contained a 20 per cent alcoholic potassium hydroxide solution. The mixture was slowly heated to 60°C and the gaseous vinyl bromide evolved was bubbled through water at 25°C to remove entrained alcohol. When gas evolution slackened, the alcoholic potassium hydroxide solution was heated to boiling. The vinyl bromide was trapped

---

10. A. L. Henne and M. W. Renoll, J. Am. Chem. Soc., 58, 887 (1936).
11. C. P. Smyth, R. W. Dornte, and E. B. Wilson, Jr., J. Am. Chem. Soc., 53, 4242 (1931).
12. C. L. Wilson and A. W. Wylie, J. Chem. Soc., 601 (1941).
13. F. Swarts, Bull. Acad. roy. Belgique, 383 (1901); Chem. Zentral., 2, 804 (1901).

in an ice bath and redistilled twice before use, the second time from magnesium sulfate. It was stored in a brown bottle at 8°C.

Dioxane.--Dioxane was purified by the method described by Fieser (14). A mixture of 4 l. of commercial dioxane, 55 ml. of concentrated hydrochloric acid and 400 ml. of water was refluxed 12 hours during which time a slow stream of nitrogen was bubbled through the solution to entrain acetaldehyde. The solution was cooled and potassium hydroxide pellets added slowly until a saturated solution was formed. The dioxane layer was decanted, shaken with potassium hydroxide pellets to remove more water, decanted into a clean flask, and refluxed with sodium 12 hours. The dioxane was poured into a clean 5 l. flask along with the remaining sodium. Boiling chips were added and the liquid distilled through a glass-helix packed, vacuum-jacketed column. The b.p. was 100-101°C at 739 mm. That reported in the literature (15) is 101.3°C.

Sodium Hydroxide Solution.--A 50 per cent aqueous solution of sodium hydroxide, made by dissolving commercial C.P. grade sodium hydroxide pellets in water, was filtered through a medium mesh fritted glass funnel to remove undissolved carbonates. The filtrate was diluted to approximately the desired concentration and standardized against hydrochloric acid solution which in turn had been standardized against sodium carbonate.

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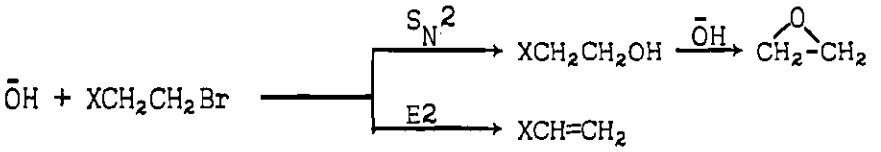
14. L. F. Fieser, Experiments in Organic Chemistry, Part II, 2nd Ed., D. C. Heath and Co., New York, N.Y., 1941, p. 369.

15. E. R. Smith and M. Wojciechowski, J. Res. Natl. Bur. Stan., 18, 461 (1937).

CHAPTER III

RESULTS

The comparison of the effect of one halogen on the reactivity of another halogen atom in the same molecule involved the compounds beta-fluoroethyl bromide, beta-chloroethyl bromide and beta-bromoethyl bromide. beta-Iodoethyl bromide was not studied because the beta-iodo substituent would be expected to be removed by nucleophilic attack at a rate comparable to that of beta-hydrogen removal (6). The comparison consisted of a study of the kinetics of the reactions of the three halogen compounds with sodium hydroxide in 50 volume per cent aqueous dioxane solution. The reaction may follow either of two possible paths, substitution (S_N2) or elimination (E2) (1).



It can be seen from the equation that in the reaction involving initial substitution, a total of two moles of hydroxide is eventually used per mole of organic halide since the intermediate halohydrin, XCH_2CH_2OH, is very reactive toward base under the conditions used. The data of Stevens, McCabe, and Warner (16, 17) show that the reactivities of the halohydrins

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16. J. E. Stevens, C. L. McCabe, and J. C. Warner, J. Am. Chem. Soc., 70, 2449 (1948).
17. C. L. McCabe and J. C. Warner, ibid., 70, 4031 (1948).

are great enough for them to be treated as reactive intermediates whose concentrations never become comparable to those of the reactants or products.

The reactivity of vinyl bromide under the conditions of the dihalide reactions was found to be much less than that of the dihalides (Table 1). Vinyl fluoride and vinyl chloride, the elimination products from beta-fluoroethyl bromide and beta-chloroethyl bromide, would certainly be less reactive than vinyl bromide toward base. It has been assumed that in the E2 reaction in all three compounds the bromine is lost rather than chlorine or fluorine due to the greater reactivity of bromine in such reactions. Thus, the overall reaction rate will be

$$v = k_{E2}[RBr][\bar{O}H] + k_{S_N2}[RBr][\bar{O}H] \quad . \tag{1}$$

and if f is the fraction of the reaction going by the S_N2 path, then

$$\frac{dx}{dt} = k_2(a - x)[b - (1 + f)x] \tag{2}$$

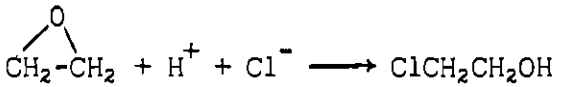
where $a = [RBr]_0$, $b = [\bar{O}H]_0$, $x = [RBr]$ lost at time t, k_2 = overall reaction rate constant, $k_2 f = k_{S_N2}$ and $k_2(1 - f) = k_{E2}$. Integration of this equation by the method of partial fractions gives

$$k_2 = \frac{2.303}{t[b - (1 + f)a]} \log \frac{a[b - (1 + f)x]}{b(a - x)} \quad . \tag{3}$$

Attempts to determine the value of f experimentally by allowing an excess of base to react completely with the halogen compound and using the equation, $f = (a - b)/b$, where a is the moles of sodium hydromide used when reaction is complete and b is the moles of sodium hydroxide used if no substitution occurs, were unsuccessful. Apparently

the slow reaction of the vinyl halide used up base causing the rate constants calculated by equation (3) to decrease as the reaction time increased.

Another attempt was made to determine f by analysing quantitatively for ethylene oxide produced in the substitution reaction. The method of Lubatti (18) in which the ethylene oxide is distilled from the reaction mixture into a saturated aqueous magnesium chloride solution containing a known concentration of hydrochloric acid was used. The high chloride ion concentration aids the addition of hydrochloric acid to the oxide.



$$CH_2\text{-}CH_2 + H^+ + Cl^- \longrightarrow ClCH_2CH_2OH \qquad (5)$$

Since one mole of hydrochloric acid is used up per mole of oxide, titration with base indicated the moles of oxide present. The method worked fairly well except it apparently was difficult to achieve complete recovery of ethylene oxide from the aqueous dioxane solution. Also, according to the data of Lichtenstein and Twigg (7), ethylene oxide is hydrated (in the reaction mixture) to ethylene glycol at a rate which was comparable to the reaction rates obtained in the present work.

Attempts to hydrate the ethylene oxide in the oxide-glycol mixture and determine the total glycol content by oxidation with hydrochloric acid (8) proved to be unsuccessful. This was shown to be due to interference by bromide ion which is oxidized to bromine and/or higher oxidation states under the conditions used.

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18. O. F. Lubatti, J. Soc. Chem. Ind., 51, 361T (1932).

The f values were therefore calculated by an extrapolation carried out by taking one point past 90 per cent reaction (before an appreciable amount of vinyl halide had reacted) and choosing, by successive approximations, the value of f which gave a value of k_2 for this point equal to the average of the values calculated from the other points. This value of f was then used along with equation (3) to calculate the constants for the other points.

From k_2 and f, one may calculate, in the manner previously described, values of k_{E2} and k_{S_N2}. Data for all runs are listed in Tables 2 through 10. A summary of the rate constants along with heats and entropies of activation appear in Table 1. These were calculated using the absolute rate equation (19)

$$k = \frac{KT}{h} e^{\frac{-\Delta H^{\ddagger}}{RT}} e^{\frac{\Delta S^{\ddagger}}{R}}$$

where k_2 is the second order rate constant in l./mole-sec.; K is Boltzmann's constant, 1.38047×10^{-16} erg/deg.; h is Planck's constant, 6.624×10^{-27} erg sec.; e is the natural logarithm base; T is temperature in ^{0}A; R is the gas law constant in cal. per mole per deg.; $\Delta H^{\ddagger}$ is the heat of activation and $\Delta S^{\ddagger}$ is the entropy of activation.

It may be seen from Table 1 that the E2 rate constants are approximately 50 per cent greater for the dibromo compound (k_{E2} was divided by two for this compound to give the rate constant per bromine)

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19. S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

than for the chlorobromo compound which is about 100 times as reactive as the fluorobromo compound. This places the three halogens in the order

$$Br > Cl > F$$

with respect to their ability to facilitate removal of the beta-hydrogen.

The present values (Tables 1) calculated for k_{S_N2} do not appear to be accurate enough to indicate definitely any difference in reactivity by the S_N2 mechanism.

CHAPTER IV

DISCUSSION AND CONCLUSIONS

The two most important factors affecting the E2 reactivity in these compounds have been discussed by Ingold (20). They are: (1) the stability of the olefin being formed and (2) the acidity of the hydrogen. The steric factor discussed by Schramm (21) and Brown and coworkers (22, 23) does not seem to be important in this work because of the relatively low energy required for rotation around the carbon-carbon bond and the small size of the beta-hydrogens and the attacking base ($\bar{O}H$).

Concerning the stability of the olefin being formed, there are two ways in which the halogen atom could affect the difference in stability between the saturated starting halide and the unsaturated product. These are: (a) stabilization of the olefin by resonance and (b) stabilization of the saturated halide due to the greater electronegativity difference between halogen and saturated carbon and halogen and unsaturated carbon. These factors will now be discussed.

(a) Stabilization of the olefin by resonance. Compared to the saturated dihalide, the olefin formed from it by the E2 reaction will be stabilized by resonance of the type:

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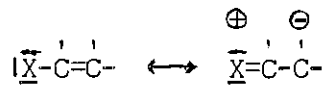
20. Ingold, op. cit., Chapter VIII.
21. C. H. Schramm, Science, 112, 367 (1950).
22. H. C. Brown and H. L. Berneis, J. Am. Chem. Soc., 75, 10 (1953).
23. H. C. Brown and I. Moritani, ibid., 75, 4112 (1953).



and due to various factors, fluorine is more effective than chlorine which is more effective than bromine in this type of resonance (24).

(b) Stabilization of the saturated halide due to the greater electronegativity difference between halogen and saturated carbon than between halogen and unsaturated carbon. Unsaturated carbon is more electronegative than saturated carbon (25). Thus, if we compare the <u>difference</u> in electronegativity between the three halogens studied when attached to the saturated carbon and to the unsaturated carbon, there will be a greater electronegativity difference between fluorine and carbon in every case since fluorine is more electronegative than chlorine or bromine. This will be true both for the saturated and unsaturated halides. Since the bond energy depends on the square of the electronegativity difference (26), the bond energy lost will be greatest for the fluoride. A calculation will bear this out. Using the equation cited by Wheland (26),

$$\triangle_{AB} = 23\ (x_A - x_B)^2 \text{ kcal./mole} ,$$

where $\triangle_{AB}$ is the bond energy between atoms A and B due to the electronegativity difference and x_A and x_B are the electronegativities of atoms A and B respectively, the bond energy due to the electronegativity

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24. Ingold, <u>op. cit.</u>, p. 75.
25. G. W. Wheland, <u>The Theory of Resonance and Its Application to Organic Chemistry</u>, 1st ed., John Wiley and Sons, inc., New York, N. Y., 1944, p. 131, 176.
26. G. W. Wheland, <u>ibid.</u>, p. 84.

difference between a saturated carbon atom and fluorine will be

$$\Delta_{AB} = 23\ (4.0 - 2.5)^2 = 51.75\ \text{kcal./mole}\ .$$

If it is assumed that the electronegativity of carbon to which fluorine is attached in vinyl fluoride is 0.1 unit greater, the bond energy will be

$$\Delta_{AB} = 23\ (4.0 - 2.6)^2 = 45.08\ \text{kcal./mole}\ .$$

Thus an electronegativity difference of only 0.1 unit decreases the bond strength by 6.67 kcal./mole. The corresponding predicted decreases in the strengths of a C-Cl and C-Br bond are 2.07 and 1.15 kcal./mole, respectively. This means that if this factor were considered alone, the vinyl fluoride would lose a greater amount of stability in its formation from the dihalide than would either vinyl chloride or vinyl bromide.

These two factors affecting olefin stability are, therefore, operating in opposite directions, the fluorine tending to stabilize the olefin more than chlorine or bromine by the resonance effect but tending to destabilize it compared to chlorine and bromine by the other effect mentioned. Patrick (27) found that fluoroolefins have higher heats of polymerization and are thus less stable than olefins having no fluorine on the double bond. For example, tetrafluoroethylene was reported to have a heat of polymerization about 16 kcal./mole greater than ethylene itself. No data of this type was given for other halogen substituted ethylenes, but it is well known that polychloro

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27. C. R. Patrick, Tetrahedron, 4, 26 (1958).

and polybromo-olefins do not have the strong tendency to undergo such additions reactions as dimerization and nucleophilic addition of alcohol characteristic of polyfluoro-olefins. This result indicates that it is probable that the bond strength lost due to electronegativity difference is of greater importance here than the resonance effect mentioned above.

Ingold (5) has attributed the activating influence of beta-halogen to the inductive effect, and Goering and Espy use the same argument to explain why bromine and chlorine increase the E2 reactivity of some 1,2-dihalocyclohexanes (4). However, Goering and Espy found bromine to be a little more effective than chlorine in this respect, and this is just opposite of what would be true if the inductive effect were the only factor. The results in Table 1 showing that fluorine reduced the E2 reactivity much more than chlorine or bromine prove that the inductive effect cannot be the controlling factor. According to these results the order is

$$Br > Cl >> F$$

with respect to facilitating removal of the beta-hydrogen by base. This order is exactly that found (28) for the ability of the halogens to facilitate carbanion formation in the base-catalyzed deuterium exchange of haloforms.

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28. J. Hine, N. W. Burske, M. Hine, and P. B. Langford, J. Am. Chem. Soc., 79, 1406 (1957).

In explaining the relative rates of carbanion formation by haloforms, three factors were considered: B-strain, d-orbital resonance, and polarizability. It seems reasonable to discuss the E2 reactivity order observed in terms of the same factors in addition to the inductive effect and olefin stability.

B-Strain. Brown (29, 30) and coworkers have developed this concept. In the formation of a carbanion by removal of a proton from a beta-dihalide, the larger halogens should facilitate carbanion formation more than the smaller ones due to repulsions between the beta halogen and the beta hydrogens. This is because the carbanion is more nearly planar than the starting molecule. However, as Hine, Burske, Hine, and Langford (28) pointed out, the replacement of chlorine by bromine produces a rather large increase in reactivity but the replacement of bromine by iodine products an almost negligible increase. Since iodine is considerably larger than bromine, it should (if B-strain were the controlling factor) produce a much higher reactivity; therefore, B-strain does not seem to be important. In the beta-haloethyl bromides B-strain should be even less important since initially there are two hydrogens attached to the carbon. It is improbable that this factor is of importance in explaining the E2 reactivity of the beta-haloethyl bromides.

d-Orbital Resonance. It is possible for resonance of the type

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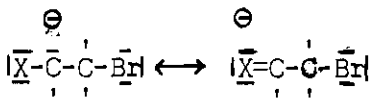
29. H. C. Brown, H. Barthalomay, Jr., and M. D. Taylor, J. Am. Chem. Soc., 66, 435 (1944).
30. H. C. Brown and R. S. Fletcher, ibid., 71, 1845 (1949).



in which the beta-halogen has ten electrons in its outer shell to facilitate the E2 reaction by dispersing the negative (or partial negative) charge on the beta carbon atom. Brehm and Levenson (31) show that divalent sulfur is more effective than divalent oxygen in its ability to promote loss of a proton from the carbon to which it is attached. Although these atoms are in a neighboring group in the periodic chart, they are perhaps somewhat comparable to the present case because in both cases the effect of neutral atoms is being measured. The greater effect of sulfur is attributed to the ability of sulfur to hold ten electrons in its outer shell. This effect is then able to overcome the stronger inductive effect of the oxygen. These workers did not investigate atoms of higher atomic number in the same group, but their results fit in with the present ones, that resonance structures involving ten electrons in the outer shell of the first period elements in both cases (F and O) are of such high energy content that they contribute almost negligibly to the total structure.

Doering, Levy, Schreiber, and Hoffmann (32, 33, 34) have found that sulfonium and phosphonium ions exchanged deuterium faster than ammonium ions and have attributed their results to the greater ease of formation of resonance structures having ten electrons by the second

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31. W. J. Brehm and T. Levenson, J. Am. Chem. Soc., 76, 5389 (1954).
32. W. E. Doering and L. K. Levy, J. Am. Chem. Soc., 77, 509 (1955).
33. W. E. Doering and K. C. Shreiber, ibid., 77, 514 (1955).
34. W. E. Doering and A. K. Hoffmann, ibid., 77, 521 (1955).

period elements (S and P). However, they found sulfur to be more effective than selenium which was more effective than tellurium. They also found a similar order in the group VA "onium" compounds. Since their results are for atoms with charges and the present ones are for neutral atoms, it is possible that this explanation does not apply here. It is interesting to note that they found the first period element, nitrogen, to be less effective than all the others and that in the present case the first period element, fluorine, was found to be less effective than the others in its ability to facilitate removal of an alpha hydrogen by base.

Polarizability. The halogens lie in the same order with respect to polarizability ($F < Cl < Br < I$) as they do with respect to their ability to promote the E2 reactions which were studied. The values listed in the literature (35) are F, 0.95; Cl, 5.967; Br, 8.865; and I, 13.900. The importance of polarizability then cannot be overlooked since in the present case a more pronounced difference in reactivity was found between fluorine and chlorine than between chlorine and bromine. This is just where the largest percentage difference occurs in polarizability.

It is impossible to tell anything definite from the present data (Table 1) from the heats and entropies of activation since the data were not accurate enough to calculate values for the E2 reactions of the fluorine compound. Furthermore, these values for the chlorine and bromine compound are within experimental error.

Slaugh and Bergman (36) investigated the deuterium exchange rates

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35. S. Smiles, The Relation Between Chemical Constitution and Some Physical Properties, Longmans, Green, and Co., London, 1910, p. 276-7.
36. L. H. Slaugh and E. Bergman, J. of Org. Chem., 26, 3158 (1961).

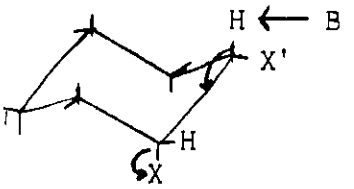
of $(C_2H_5S)_3CH$ and $(C_2H_5O)_3CH$ and found that carbanion formation was much faster in the sulfur-containing compound. These authors indicate that d-orbital resonance is probably responsible for most of the activating influence of the thioethoxy groups but that the inductive effect and polarizability cannot be excluded.

It seems then that a combination of d-orbital resonance, polarizability, inductive effect, and olefin stability is necessary to explain the order of reactivities of the compounds examined.

CHAPTER V

RECOMMENDATIONS

The work by Goering and Espy (4) is rather closely related to the present work. They studied the dehydrohalogenation of 1,2-dihalo (Cl and Br) derivatives of cyclohexane and found that the cis compounds undergo E2 reaction much faster than the corresponding trans compounds. This is because it is possible for both the hydrogen and halogen being removed to be axial and this allows the electrons to be in the proper position for double bond formation



It would be interesting to compare the E2 reactivities of cis-1-fluoro-2-bromocyclohexane, cis-1-chloro-2-bromocyclohexane and cis-1-bromo-2-bromocyclohexane and see if the same decrease in E2 reactivity is noted with the fluorine compound as noted in this work. Possibly the S_N2 reaction would be negligible and a more accurate E2 rate constant could be calculated. This would then make it possible to calculate more accurate values for heats and entropies of activation for comparison with the other values.

APPENDIX

TABLES

Method of Calculating Second Order Rate Constants. Influence of the f Value Used on the Value of the Rate Constant.

The k_2 values in Table 4 for the reaction between sodium hydroxide and ethylene fluorobromide were calculated for each point by using the equation

$$k_2 = \frac{2.303}{t[b - (1 + f)a]} \log \frac{a[b - (1 + f)x]}{b(a - x)}$$

where a is the initial halide concentration, b is the initial base concentration, x is the halide concentration lost at time t and f is the fraction of the reaction taking place by substitution. In this particular run, a = 0.01019 mole/liter and b = 0.02420 mole/liter. Using an f value of 0.79, the following values for k_2 were obtained.

time, hrs.	x	a - x	b - x	k_2
3.2333	0.001157	0.009033	0.02213	0.1612
5.9666	0.001949	0.008241	0.02071	0.1594
11.690	0.003288	0.006902	0.01831	0.1598
22.550	0.004932	0.005258	0.01537	0.1547
35.500	0.006333	0.003857	0.01286	0.1605

The average value for the above k_2 values is 0.1591 l./mole hr. with an average deviation of 1.1 per cent. Using an f value of 0.74, the average k_2 value was 0.1663 with an average deviation of 2.8 per cent. When a higher f value of 0.90 was used, the average k_2 value was 0.1385 with an average deviation of 7.1 per cent. Thus it can be seen that lower than optimum f values give higher rate constants and higher than optimum f values give lower rate constants. In both cases, the average

deviation is greater than that obtained using the optimum $\underline{f}$ value. This was found to be generally true for the other reactions investigated.

Table 2. FCH_2CH_2Br + NaOH in 50% Aqueous Dioxane at 30.0°C.

$(FCH_2CH_2Br)_o$ = 0.01039 M HCl = 0.0502 M

$(NaOH)_o$ = 0.02741 M 50 ml. aliquots

Time in Hours	ml. of HCl	10^2k(l./m.hr.)
22.850	27.10	1.534
124.10	26.40	1.326
381.17	24.37	1.548
674.83	22.20	1.702
2090.8	16.70	1.627

Average k = $(1.547 \pm 0.094) \times 10^{-2}$ l./m.hr.

= $(4.296 \pm 0.26) \times 10^{-6}$ l./m.sec.

f = 1.00

Table 3. FCH_2CH_2Br + NaOH in 50% Aqueous Dioxane at 50.1°C.

$(FCH_2CH_2Br)_o$ = 0.009369 M HCl = 0.1019 M

$(NaOH)_o$ = 0.02531 M 50 ml. aliquots

Time in Minutes	ml. of HCl	10^3k(l./m.min.)
1,589	11.40	3.054
4,220	10.04	3.132
7,263	8.79	3.280
14,301	7.15	3.184
18,907	6.38	3.249
21,537	6.00	3.326

Average k = $(3.204 \pm 0.081) \times 10^{-3}$ l./m.min.

= $(5.340 \pm 0.14) \times 10^{-5}$ l./m.sec.

f = 1.00

Table 4. FCH_2CH_2Br + NaOH in 50% Aqueous Dioxane at 70.0°C.

$(FCH_2CH_2Br)_o$ = 0.01019 M HCl = 0.1090 M

$(NaOH)_o$ = 0.02420 M 50 ml. aliquots

Time in Hours	ml. of HCl	10^3k(l./m.hr.)
3.2333	10.15	161.15
5.9666	9.50	159.37
11.650	8.40	159.79
22.550	7.05	154.65
35.500	5.90	160.54

Average k = $(159.1 \pm 1.8) \times 10^{-3}$ l./m.hr.

= $(4.416 \pm .050) \times 10^{-5}$ l./m.sec.

f = 0.79

Table 5. $ClCH_2CH_2Br$ + NaOH in 50% Aqueous Dioxane at 30.0°C.

$(ClCH_2CH_2Br)_o$ = 0.01043 M HCl = 0.1090 M

$(NaOH)_o$ = 0.01422 M 50 ml. aliquots

Time in Seconds	ml. of HCl	10^4k(l./m.sec.)
72,360	8.90	2.258
108,780	8.02	2.291
159,180	7.15	2.276
209,580	6.50	2.262
271,080	5.90	2.250
447,300	4.78	2.271

Average k = $(2.268 \pm 0.011) \times 10^{-4}$ l./m.sec.

f = 0.028

Table 6. $ClCH_2CH_2Br$ + NaOH in 50% Aqueous Dioxane at 70.0°C.

$(ClCH_2CH_2Br)_o$ = 0.01043 M HCl = 0.0485 M

$(NaOH)_o$ = 0.01422 M 50 ml. aliquots

Time in Seconds	ml. of HCl	10^2k(l./m.sec.)
900	13.16	1.264
1,890	11.87	1.247
3,120	10.61	1.259
4,380	9.56	1.295
6,240	8.49	1.249
8,490	7.65	1.242

Average k = $(1.245 \pm 0.022) \times 10^{-2}$ l./m.sec.

f = 0.03

Table 7. $BrCH_2CH_2Br$ + NaOH in 50% Aqueous Dioxane at 30.0°C.

$(BrCH_2CH_2Br)_o$ = 0.008914 M HCl = 0.0970 M

$(NaOH)_o$ = 0.01455 M 50 ml. aliquots

Time in Hours	ml. of HCl	k(l./m/hr.)
5.200	6.70	2.519
12.400	6.00	2.319
22.683	5.20	2.392
26.333	5.00	2.377
35.766	4.55	2.400
45.983	4.20	2.398
49.783	4.08	2.420
53.050	4.02	2.377

Average k = 2.400 ± 0.035 l./m.hr.

= 6.667 ± 0.098 x 10^{-4} l./m.sec.

f = 0.05

Table 8. $BrCH_2CH_2Br$ + NaOH in 50% Aqueous Dioxane at 70.0°C.

$(BrCH_2CH_2Br)_o$ = 0.008531 M HCl = 0.0970 M

$(NaOH)_o$ = 0.008540 M 50 ml. aliquots

Time in Seconds	ml. of HCl	10^2k(l./m.sec.)
823	6.90	3.790
1,205	6.29	3.798
1,760	5.54	3.673
2,480	4.74	3.826
3,275	4.14	3.836
4,170	3.59	3.773

Average k = $(3.783 \pm 0.040) \times 10^{-2}$ l./m.sec.

f = 0.05

Table 9. H_2C=CHBr + NaOH in 50% Aqueous Dioxane at 75°C[a].

$(CH_2=CHBr)_o$ = 0.01038 M HCl = 0.0502 M

$(NaOH)_o$ = 0.02774 M 50 ml. aliquots

Time in Hours	ml. of HCl	k(l./m.hr.)
3.233	26.58	0.986
19.78	22.80	1.002

Average k = 0.994 ± 0.18 l./m.hr.

= (2.7 ± 0.5) x 10^{-4} l./m.sec.

[a]Temperature was 75 ± 2°C.

Table 10. CH_2=CHBr + NaOH in 50% Aqueous Dioxane at 30.0°C.

$(CH_2=CHBr)_o$ = 0.01063 M HCl = 0.0502 M

$(NaOH)_o$ = 0.02779 M 50 ml. aliquots

Time in Hours	ml. of HCl	10^3k(l./m.hr.)
72.27	27.60	5.147
171.17	27.50	3.960
333.58	27.33	3.358
719.95	26.95	3.890

Average k = $(4.088 \pm 1.44) \times 10^{-3}$ l./m.hr.

= $(1.135 \pm 0.40) \times 10^{-6}$ l./m.sec.

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Part II

THE BASE CATALYSED DEHYDROHALOGENATION OF *beta*-BENZENE HEXACHLORIDE

SUMMARY

PART II

The rates of deuterium exchange of deuterio-m-difluoro-, deuterio-m-chlorofluoro-, deuterio-m-dichloro- and deuterio-1,2,4-trichlorobenzenes have been studied in methanol solvent at various temperatures. Fluorine is more effective than chlorine in facilitating deuterium exchange and rates of deuterium exchange of the compounds studied lie in the following order

$$C_6H_3F_2D > C_6H_2Cl_3D > C_6H_3ClFD > C_6H_3Cl_2D .$$

This order is explained in terms of inductive and field effects.

Additional evidence has been found indicating that beta-benzene-hexachloride (cis-1,3,5-trans-2,4,6-hexachlorocyclohexane) undergoes basic dehydrochlorination by a carbanion (ElcB) mechanism. Other workers had previously determined that the unreacted starting material contained some deuterium when allowed to react with base in "heavy" ethanol. In the present study, the product (1,2,4-trichlorobenzene) of the reaction between beta-benzene hexachloride and sodium methoxide in "heavy" methanol was found to contain considerable deuterium. Since, under the same conditions, deuterio-1,2,4-trichlorobenzene was found to exchange deuterium for hydrogen about 100 times slower than the elimination reaction, the product could not have gotten the deuterium after it was formed. These results indicate that beta-benzene hexachloride reacts with sodium methoxide in methanol by the ElcB mechanism. The halide first reacts with the methoxide to give a carbanion of beta-

benzene hexachloride. This carbanion inverts to give the carbanion of delta-benzene hexachloride (1,2,3,5-cis-2,6-trans-hexachloro-cyclohexane) which abstracts deuterium from the solvent, forming delta-benzene hexachloride. Since the delta isomer has H and Cl atoms in a trans position, elimination occurs leaving deuterium attached to the doubly bonded carbon. Two cis eliminations then give the deuterio-1,2,4-trichlorobenzene.

CHAPTER I

INTRODUCTION

The present work was undertaken in order to obtain more information concerning the ability of various halogen atoms on the benzene nucleus to facilitate carbanion formation and to obtain additional information about the mechanism of the base-catalyzed dehydrochlorination of beta-benzene hexachloride. The two aspects of the work are closely related because 1,2,4-trichlorobenzene is the major product of the dehydrochlorination reaction (1).

m-Difluoro, m-chlorofluoro, m-dichloro, and 1,2,4-trichlorobenzene were studied to determine their rates of exchange of deuterium for hydrogen. The dihalides were studied, in addition to the trihalide, to learn more about the effect of different halogens in facilitating carbanion formation in aromatic compounds. The deuterium exchange rate of fluorobenzene, trifluoromethylbenzene, anisole, toluene, and benzene had previously been studied under rather drastic conditions (2) (0.6 M KNH_2 in NH_3) but apparently no similar study had been made of the m-dihalobenzenes mentioned above. The deuterium exchange rate of 1,2,4-trichlorobenzene was determined because it is directly involved in the in the interpretation of the experimental results obtained in investigating the mechanism of the dehydrohalogenation of beta-benzene hexachloride.

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Bimolecular dehydrohalogenation can occur by either of two mechanisms, a concerted one (E2) or a stepwise one (ElcB). In the concerted mechanism, the base attacks the hydrogen on the carbon adjacent to the one bearing the halogen provided the hydrogen and halogen can assume positions trans to each other (3). The concerted trans reaction is usually favored in the reactions of saturated halides if it is stereochemically possible (4).

In the carbanion mechanism, the base first removes the hydrogen from the carbon adjacent to the one bearing the halogen. This forms a carbanion which then loses a halide ion forming the product (1).

It is often possible to use two methods to distinguish the two mechanisms. One can test for general base catalysis or one can run the reaction in a deuterated solvent and test the product or unreacted starting material for deuterium content. A positive test for deuterium would indicate that in the carbanion mechanism the first step is reversible and thus would indicate carbanion formation. In investigating the dehydrohalogenation of beta-benzene hexachloride deuterium exchange with the solvent has been chosen to test for carbanions.

Deuterium exchange has usually not been found to occur in dehydrogalogenating compounds such as beta-phenylethyl bromide and 2-ethylbutyl bromide-2d, where the hydrogen being removed can be trans to the leaving halide (5). It has, however, been observed in compounds

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such as trichloroethylene (6) where the hydrogen is trans to a chlorine, and beta-benzene hexachloride (7) where the hydrogen cannot assume a trans position. The combination of all cis H-Cl pairs and relatively strongly electron-withdrawing groups in beta-benzene hexachloride make this compound an excellent one to test for carbanion formation. Since Cristol (7) found some deuterium in the unreacted starting material when dehydrochlorinating this compound in "heavy" ethanol, it was decided to reinvestigate the system by testing the product for deuterium content as suggested by Cram (8). The loss of the last two moles of hydrogen chloride from the compound is very fast (4) compared to that of the first mole and, therefore, it seems unlikely that any deuterium observed in the product would have been picked up by one of the intermediate compounds.

Another possibility is that deuterium could be picked up by the product after it was formed. To investigate the possibility it was decided to determine the rate of deuterium exchange of 1,2,4-trichlorobenzene under the conditions used in the elimination reaction.

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CHAPTER II

PROCEDURE

Experimental

Kinetics of the Exchange Reactions Between Deuterio Di- and Trihalobenzenes and Sodium Methoxide in Methanol.--The exchange reactions of the deuterium derivatives of m-difluoro, m-chlorofluoro, m-dichloro, and 1,2,4-trichloro-benzene in methanol were all carried out in essentially the same manner. The operation for obtaining each point will be described for the deuterio-m-difluorobenzene.

Ten microliters of the deuterium-substituted halogen compound (measurement made with a syringe calibrated to 0.2 microliter) was added to a 12 ml. vial. Ten ml. of 0.09932 M sodium methoxide in methanol was pipetted into the vial and, after carefully removing any solution adhering to the inside of the opening, the vial was sealed. During the entire operation care was taken to introduce the liquids into the vial in such a manner that as little liquid as possible remained on the inside sealing surface of the neck of the vial. After sealing, the vial was carefully inspected for any discoloration inside the neck which would indicate decomposition of the contents. No discoloration was noted. The vial was placed in the appropriate constant temperature bath for a measured length of time, removed, and quickly cooled with tap water. Then, before opening, the outside of the vial was washed twice with soap and rinsed thoroughly to remove any impurities from it.[1] The entire cooling and washing

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[1] This procedure was necessary because a light mineral oil was used for the bath liquid in the runs at 50° and 70°C.

operation took 1-1.5 minutes. The sealed tip of the vial was then broken and the contents poured into a glass stoppered flask containing 20 ml. of 0.1044 M perchloric acid solution to neutralize the base and stop the deuterium exchange. Then 4 ml. of carbon disulfide was added and the flask was thoroughly shaken several times to insure complete extraction, allowing two or three minutes between shakings for the layers to separate. The carbon disulfide layer was removed with a syringe, placed in a 10 ml. Erlenmeyer flask, and then immediately poured into another 10 ml. Erlenmeyer flask containing dry indicating silica gel. This procedure was found to be very effective in removing the water-alcohol droplets in the carbon disulfide extract because many of these droplets adhered to the walls of the flask in which the extract was first placed. The carbon disulfide extract was then examined at the appropriate wavelengths (see Table 12) for deuterium and hydrogen content.

The extraction procedure described above was found to be very efficient. One of the samples thus extracted was extracted again with 4 ml. of carbon disulfide. This carbon disulfide layer was separated and dried as before. The infrared spectrum between 2 and 15 microns indicated negligible absorption.

Times recorded for these runs (Tables 2 through 9) were measured using an electric clock with second hand.

The constant temperature bath used for the 50° and 70° runs was constant to $\pm$ 0.1°C. A light mineral oil was used for the bath liquid to prevent temperature fluctuations due to evaporation losses from the bath.

Refluxing water was used for the constant temperature bath at 100°C.

Kinetics of the Reaction Between beta-Benzene Hexachloride and Sodium Methoxide in Methanol.--A 0.01989 M solution was made by dissolving a weighed quantity of the halide in absolute methanol. The solubility in methanol is quite low and the halide dissolves very slowly. Solution was finally accomplished by adding the halide to about 50 ml. of methanol in a 100 ml. volumetric flask and alternately heating, stirring, and adding methanol until all of the halide dissolved and the flask contained 100 ml. of solution.

Each point in the run was determined in the following manner: Five milliliters of the halide solution was pipetted into a 12 ml. vial and 0.50 ml. of 0.9895 M sodium methoxide in methanol was added by syringe. Any liquid adhering to the inside of the top to be sealed was carefully removed and the vial sealed. The vials were then placed in the appropriate constant temperature bath for a measured length of time and on removal were quickly cooled with tap water. Since times were relatively long in the run at 70°, satisfactory rate constants were obtained by opening the vial, pouring contents (along with 2 rinse solutions) into an Erlenmeyer flask, and immediately titrating with standard HCl. In the run at 100°, the vial contents and rinse solutions were poured into excess standard hydrochloric acid solution and back titrated with sodium hydroxide solution. These results are recorded in Tables 10 and 11.

Times reported in hours were measured using an electric clock with second hand. Those in seconds were measured with an electric timer calibrated in tenths of seconds.

Reaction Between beta-Benzene Hexachloride and Sodium Methoxide in CH_3OD at 100°C.--Due to the limited availability of methanol-d (CH_3OD) and

because only one reaction was necessary, a procedure different from the one previously described for kinetic runs between beta-benzene hexachloride and sodium methoxide was used. Five ml. of methanol-d was pipetted into a 12 ml. vial that contained 0.0296 g. ($_{o}$.102 millimoles) of beta-benzene hexachloride. In order to dissolve the halide without loss of methanol-d the vial was sealed and placed in a bath at 100° for about one hour. The vial was shaken occasionally during this time. Then to start the reaction, the vial was removed from the bath, cooled, washed with soap, rinsed twice, and opened. One-half milliliter of 1.303 M sodium methoxide in methanol-d was added by syringe. The vial was resealed and heated at 100° for 25 minutes. This time corresponds to about 95 per cent reaction. The contents were cooled and 2 ml. of water added to prevent mixing with the carbon disulfide extracting liquid. Two milliliters of carbon disulfide was added, the contents were shaken vigorously several times, and the carbon disulfide layer was drawn off. This carbon disulfide layer (after drying with silica gel) was examined spectrophotometrically. See Figure (8) for results.

Preparation and Purification of Reagents

m-Difluorobenzene.--Pierce Chemical Co. m-difluorobenzene was used without further purification. The refractive index (n_D^{29}, 1.4339; n_D^{21}, 1.4379) compares favorably with that reported in the literature (n_D^{18}, 1.4404) (9).

Deuterio-m-Difluorobenzene.--Six tenths milliliter of m-difluorobenzene and 2.40 ml. of 1.327 M sodium methoxide in methanol-d were sealed in a

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9. G. Schiemann and R. Pillarsky, Ber., 62, 3035 (1930).

vial having a total volume of 12 ml. The vial was placed in a 50° bath for 97 hours at which time it was removed and thoroughly washed with soap and water. The contents were added to a 3 ml. of water in a 10 ml. Erlenmeyer flask and vigorously shaken to remove methanol and base from the halide layer. This layer was separated and again treated with 3 ml. of water. After vigorous shaking, the halide layer was separated and dried with a small quantity of silica gel. About 0.45 ml. of product was obtained which had a slight straw color. This color disappeared after standing overnight.

m-Chlorofluorobenzene.--Distillation Products Industries White Label m-chlorofluorobenzene was used without further purification. The refractive index (n_D^{29}, 1.4909) compares favorably with that reported in the literature (n_D^{27}, 1.4911) (10).

Deuterio-m-Chlorofluorobenzene.--Six-tenths of a milliliter of m-chlorofluorobenzene and 2.40 ml. of 1.327 M sodium methoxide in methanol-d were sealed in a 12 ml. vial and heated for 18 hours at 100°C. The product was separated and purified in exactly the same manner as the deuterio-m-difluorobenzene described above. About 0.45 ml. of clear liquid product was obtained.

m-Dichlorobenzene.--Distillation Products Industries White Label m-dichlorobenzene was used without purification. The refractive index (n_D^{29}, 1.5430) compares favorably with that in the literature (n_D^{30}, 1.5420) (11).

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10. H. S. Booth, H. M. Elsey, and P. E. Burchfield, J. Am. Chem. Soc., 57, 2064 (1935).

11. S. S. Joshi and G. D. Tuli, J. Indian Chem. Soc., 28, 450 (1951).

Deuterio-m-Dichlorobenzene.--Six-tenths of a milliliter of m-dichlorobenzene and 2.40 ml. of 1.327 M sodium methoxide in methanol-d were sealed in a 12 ml. vial and heated for 68 hours at 100°C. The product was separated and purified in the same manner as the deuterio-m-difluorobenzene described above. About 0.40 ml. of clear product was obtained.

1,2,4-Trichlorobenzene.--Distillation Products Industries White Label 1,2,4-trichlorobenzene was distilled and dried over silica gel. The product was clear and melted at 16-17°C. The value reported in the literature is 17-18° (12). The refractive index (n_D^{27}, 1.5685) compares favorably with that in the literature (n_D^{20}, 1.5714) (11).

Deuterio-1,2,4-Trichlorobenzene.--Three-fourths of a milliliter of redistilled 1,2,4-trichlorobenzene and 3.00 ml. of 1.303 M sodium methoxide in methanol-d were sealed in a 12 ml. vial and heated for 10 hours at 100°C. The product was purified in the same manner as the deuterio-m-difluorobenzene described above. About 0.55 ml. of clear product was obtained.

1,3,5-Trichlorobenzene.--Distillation Products Industries White Label 1,3,5-trichlorobenzene was used without additional purification. The melting point, 62-3°, compares favorably with the 63° value found by Olivier (13).

beta-Benzene Hexachloride.--This compound was obtained from E. I. Du Pont de Nemours and Co., Inc. and was used without further purification. The melting point, 304-5°, falls within the range of values (297° to 312°) reported in the literature (14).

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12. S. C. J. Olivier, Rec. trav. chim., 39, 499 (1920).
13. S. C. J. Olivier, Rec. trav. chim., 37, 313 (1918).
14. E. H. Huntress, Organic Chlorine Compounds, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 505-6.

Methanol.--Commercial methanol was purified by the method of Fieser (15). Two and one-half liters of methanol was placed in a 5 liter flask which was fitted with a reflux condenser. Several grams of magnesium turnings was added and the mixture refluxed for two hours. A 30 x 3/4 inch, vacuum jacketed, glass helix packed distilling column was attached and the distillate boiling at 64.5 to 65.0°C was collected. Special care was taken to attach the receiving bottle to the condenser in such a way that water vapor from the air could not contaminate the distillate.

Methanol-d.--This compound, CH_3OD, was obtained from Merck, Sharpe, and Dohme of Canada, Limited, and was used without further purification. The indicated isotopic purity was 99 per cent. Nuclear magnetic resonance spectra of this material and of various mixtures of it with purified "light" methanol were made to check the isotopic purity[1]. It was found that the commercial product contains only 95.1 per cent methanol-d.

Carbon Disulfide.--Baker Analysed, Reagent Grade, carbon disulfide was used after drying over silica gel.

Sodium Methoxide Solution.--The approximately 1 M sodium methoxide solutions in methanol or methanol-d were made by weighing out carefully freshly cut pieces of sodium and adding to the appropriate alcohol.

Isotopic Analysis

In order to analyse quantitatively for the protium and deuterium compounds studied, a Perkin Elmer Model 21 Infrared Spectrophotometer was used.

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15. L. F. Fieser, Experiments in Organic Chemistry, 3rd ed., D. C. Heath and Co., Boston, Mass., 1955, p. 289.

[1]The author is grateful to Mr. James Houston and Mr. Roy Duckett for the n. m. r. analysis.

For the protium compounds absorption bands that would be useful in quantitative analysis were determined for each halogen compound (m-difluoro, m-chlorofluoro, m-dichloro, and 1,2,4-trichlorobenzene) in the following manner. The spectrum for the pure protium compound was determined in carbon disulfide[1] solution at a concentration such that the optical density did not exceed 0.90 at any wavelength. Then three vials were prepared, each containing a small quantity of the "light" halide and a solution of sodium methoxide in methanol-d. These were allowed to react for different lengths of time at a suitable temperature such that deuterium exchange with the solvent occurred. The spectra of the carbon disulfide extract of the vial contents were examined and an absorption band present in the pure halide which progressively decreased in the presence of the sodium methoxide-methanol-d was selected as the one useful in analysing for the protium compound. It was possible in every case to find an absorption band suitably separate from the others, which could be used for analysis of the kinetic run mixtures.

In order to select a suitable band for use in the deuterium analysis, the spectra mentioned above were examined for bands not present in the pure protium compound. A band was then selected that increased in intensity with increasing reaction time for each of the three vials. Again in every case it was possible to find an absorption band at a wavelength at which the absorption of the protium compound

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[1]Carbon disulfide was selected as the solvent because it was found not to absorb in the infrared region at wavelengths useful in these analyses. In addition it is insoluble in methanol and could be used to extract the halogen compounds from methanol solutions used in kinetic runs.

is negligible and which was suitable for use in analysis.

Exact wave lengths for both the protium and deuterium absorption bands reported in Table 22 were determined in the following manner. A solution of the protium or deuterium compound in carbon disulfide was made up to such a concentration that the optical density at the wave length under investigation was between 0.2 and 0.6. The drum drive gears on the instrument were changed to give a scale reading of 80 inches/micron. The wave length was then set at a slightly lower value than maximum absorption and gradually increased. The absorption maximum appeared as a plateau instead of a peak and the midpoint of the plateau was taken as the wavelength of maximum absorption.

Determination of Extinction Coefficients and Isotopic Purity

The method of determining the extinction coefficients and isotopic purities for the halogen compounds will be illustrated for the case of 1,2,4-trichlorobenzene.

An expression of Beer's Law was used.

$$O.D. = \epsilon \, l \, C \, , \qquad (1)$$

where O.D. is the optical density, ϵ is the molar extinction coefficient, l is the cell length in centimeters, and C is the solute concentration in moles/liter. The designation ϵ_H refers to the extinction coefficient of the "light" halide at the hydrogen wave length and ϵ_D to that of the deuterio halide at the deuterium wavelength.

To obtain ϵ_H for 1,2,4-trichlorobenzene, two samples of the purified compound were prepared by dissolving 10 microliter of the purified "light" halide in 1.50 ml. of carbon disulfide. The optical density of each

solution was then determined at 9.135 microns. The values for the two solutions were identical, 0.444. The molarity of the two solutions was

$$M = \frac{(D)(ml.)/M.W.}{V} = \frac{1.446 \times 0.010/181.46}{0.00150} = 0.05312 \qquad (2)$$

and the extinction coefficient was

$$\epsilon_H = \frac{O.D.}{1XC} = \frac{0.444}{0.05 \times 0.05312} = 167.2 \qquad (3)$$

Since no pure sample of deuterio-1,2,4-trichlorobenzene was available, ϵ_D was determined from the isotopically impure deuterio compound in the following manner. Two solutions, each containing 20 microliter of the halide in 0.75 ml. of carbon disulfide, were prepared. The molarity of the total halogen compound in each solution was therefore 0.2125 (Equation 2). It was assumed that there was no absorption due to the pure deuterium compound at the hydrogen wave length, 9.135 microns. Even if this assumption is not valid, it has been shown by Hine, Burske, Hine, and Langford (16) for the case of deuterio-haloforms that the values of k are completely independent of the validity of the assumption that the pure deuterium compound does not absorb at the protium wave length maximum. This was done by showing that the ratio of the true fraction of deuteration to the value used for the fraction is a constant, independent of the haloform concentration and of the true value of the extent of deuteration. Optical densities were then determined for the two solutions at this wave length and the average value was 0.230. The protium compound concentration in the mixture is, therefore,

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16. J. Hine, N. W. Burske, M. Hine, and P. B. Langford, J. Am. Chem. Soc., 79, 1406 (1957).

$$C_H = \frac{O.D.}{1\ \epsilon_H} = \frac{0.230}{0.05 \times 167.2} = 0.02751 \text{ mole/liter},$$

since

$$C_{Total} = C_D + C_H ,$$

$$C_D = 0.2125 - 0.02751 = 0.1850 \text{ mole/liter}$$

The optical densities at the deuterium wave length, 8.430 microns, for the two solutions above averaged 0.312. Therefore,

$$\epsilon_D = \frac{O.D.}{1\ C_D} = \frac{0.312}{0.05 \times 0.1850} = 33.73 .$$

Using C_D and C_H, the fraction deuterium compound in the mixture was

$$p = \frac{C_D}{C_D + C_H} = \frac{0.1850}{0.1850 + 0.02751} = 0.8706 .$$

Method of Determining Hydrogen to Deuterium Ratio in Kinetic Runs.

In the kinetic runs it was not necessary to determine the individual concentrations of the hydrogen and deuterium compounds but only the ratio of the two concentrations, C_H/C_D. The base-catalyzed deuterium exchange reactions studied follow pseudo first order kinetics since the base is not used up and its concentration remains constant. Using an equation derived by Hine, Peek, and Oakes (17),

$$k_1 = \frac{2.303}{t} \log \left[p_o + p_o \left(\frac{C_H}{C_D}\right)\right] , \qquad (4)$$

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17. J. Hine, R. C. Peek, Jr., and B. D. Oakes, J. Am. Chem. Soc., 76, 827 (1954).

and knowing the fraction of deuterium in the starting material, p_0, a plot of t versus the log factor in equation (4) should give a straight line with slope equal to 2.303/k. Thus the rate constant was calculated by substituting the value of the graphically determined slope into

$$k_1 = \frac{2.303}{\text{slope}} .$$

The method of determining p_0 (see page 50) has been described. The C_H/C_D was determined for each point in the kinetic runs by infrared analysis of the carbon disulfide extract of the reaction mixture. In order to do this, a base line was first run by placing carbon disulfide in each of the 0.05 cm. cells and recording the absorption, if any, at the wave lengths to be used for analysis of the hydrogen and deuterium compounds. The carbon disulfide extract was then placed in the solution cell and the wave length set at a value slightly lower than the predetermined maximum absorption wave length. The drum drive gears were changed to give a scale reading of 80 inches/micron and the wave length slowly increased until maximum absorption occurred. In all cases the maximum absorption occurred at or very near the maximum absorption wave length previously determined. The wavelength was then run back to a value less than the maximum absorption value and slowly increased until the exact desired wave length was reached. The drum was then disconnected from the wave length drive and turned slowly until the indicated optical density stabilized. Then the base line absorption, if any, was subtracted from this to get the absorption due to the compound itself. The procedure was repeated at the wave length of the other (H or D) absorption. The equation used to calculate C_H/C_D from the optical densities can be derived

as follows.

$$D_H = \epsilon_H l\, C_H \tag{5}$$

$$D_D = \epsilon_D l\, C_D \tag{6}$$

Solving each for l and setting the two equal one gets:

$$\frac{D_H}{\epsilon_H C_H} = \frac{D_D}{\epsilon_D C_D}$$

from which

$$\frac{C_H}{C_D} = \frac{D_H \epsilon_D}{D_D \epsilon_H} \cdot \tag{7}$$

Values thus calculated are recorded in Tables 12 through 19.

Method of Calculating Rate Constants for Dehydrohalogenation of beta-Benzene Hexachloride.

Since three moles of base are used per mole of halide, the rate expression is

$$\frac{dx}{dt} = k_2(a - x)(b - 3x)$$

where x is the change in halide concentration, at time t, a is the initial halide concentration and b is the initial base concentration. This can be integrated to give

$$k_2 = \frac{2.303}{t(b - 3a)} \log \frac{3a(b - 3x)}{b(3a - 3x)} \tag{8}$$

which rearranges to

$$t = \frac{2.303}{k_2(b - 3a)} \log \frac{3a(b - 3x)}{b(3a - 3x)} \qquad (9)$$

It can be seen that a plot of t versus the log factor should give a straight line with slope $2.303/k_2(b - 3a)$. In practice the best line was drawn through the points plotted from the data in Tables 10 and 11 and the slope thus determined used to calculate k_2:

$$k_2 = \frac{2.303}{\text{slope}(b - 3a)} \cdot \qquad (10)$$

See Figure (2) for a plot of the data in Table 10: Dehydrohalogenation of beta-Benzene Hexachloride at 70°C.

CHAPTER III

RESULTS

The results obtained for the relative effect of halogens on the rate of deuterium exchange of the deuterio di- and trihalobenzenes are summarized in Table 1. The reactions follow pseudo first-order kinetics and for the dihalo compounds, can be written,

$$C_6H_3X_2D + \bar{O}CH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_6H_3X_2^- + DOCH_3 \qquad (11)$$

$$C_6H_3X_2^- + HOCH_3 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C_6H_3X_2H + \bar{O}CH_3 \qquad (12)$$

An integrated form of the first order rate equation

$$k_1 = \frac{2.303}{t} \log \left[p_o + p_o\left(\frac{C_H}{C_D}\right) \right] \qquad (13)$$

has been described in Chapter II and the reactions studied gave acceptably precise rate constants when k_1 was determined from the slope of the line obtained by plotting t versus the log term in equation (13). No really significant deviations from linearity were found in these plots even though in most cases the reactions were followed beyond 50 per cent completion. The largest deviations were found with the deuterio-*m*-dichlorobenzene at both temperatures used, 100° and 120°C. Both reactions

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* Since the reactions were run in pure CH_3OH solvent, k_{-1} will be negligible and k_2 will be comparatively large.

were followed to about 55 per cent completion and the last point in both cases was a little low, indicating the possibility of a complication after 50 per cent reaction. This deviation is not serious, however, since in both cases the error estimated graphically was about $\pm$ 4 per cent. In addition, the points for these two runs were somewhat more erratic than the others and the apparent downward trend may not be real[1].

Some difficulty was experienced in obtaining the p_0 value (fraction deuterium in the deuterio compound at zero time) for the m-difluoro compound. With all the other compounds studied the values obtained in the original isotopic analysis (Chapter II, p. 50) were used. However, in this case it was necessary to make up solutions for points exactly like those used in obtaining points at time t except that immediately after sealing the vials they were opened and examined spectroscopically for deuterium and hydrogen content. This technique gave a lower value (0.674 vs. 0.749) for p_0 but did give a straight line which went through the origin when the curve was drawn. This seemed to be a better method since the curve must go through the origin if the kinetics obey equation (13).

It can be seen from Table 1 that the compounds lie in the order

$$C_6H_3F_2D > C_6H_2Cl_3D > C_6H_3ClFD > C_6H_3Cl_2D$$

with respect to the rate of deuterium exchange. Thus two ortho fluorine atoms are almost 50 times as effective as two ortho chlorine atoms in

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[1] None of the deviations observed can be attributed to a second order reaction using up base. This possibility was tested experimentally and after 50 per cent exchange, the quantity of base in the reaction mixture had not decreased.

facilitating removal of deuterium. The addition of a third chlorine to m-dichlorobenzene still does not overcome this effect.

It was of particular interest to determine the rate of deuterium exchange for the 1,2,4-trichlorobenzene since it is the major product in the base-catalysed dehydrohalogenation of beta-benzene hexachloride (1). In this isomer of 1,2,3,4,5,6-hexachlorocyclohexane, all chlorine atoms are trans to each other, and it is apparently impossible for it to undergo dehydrohalogenation by the ordinary E2 mechanism. Cristol and Fix (7) carried out the dehydrohalogenation of this compound using C_6H_5OD (70 per cent isotopic purity) solvent and , after 50 per cent reaction, could not detect deuterium in the unreacted starting material using infrared analysis. They did, however, detect a small but significant amount of deuterium in the unreacted halide by use of the mass spectrometer. They found that about 0.08 per cent of the halide molecules recovered contained deuterium in place of hydrogen after correcting for the natural hydrogen to deuterium ratio.

Their results could be explained by assuming that a carbanion was formed from the beta-benzene hexachloride and that this carbanion abstracted deuterium from the solvent.

It was decided to investigate the products (1,2,4- and 1,3,5-trichlorobenzene) of the reaction for deuterium content rather than attempting to investigate the recovered starting material. This was done by allowing a weighed quantity of beta-benzene hexachloride to react with sodium methoxide in 99 per cent CH_3OD (see Chapter II, p.44 for details) to about 95 per cent completion. The infrared spectrum of the carbon

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7. S. J. Cristol and D. D. Fix, J. Am. Chem. Soc., 75, 2647 (1953).

disulfide extract of this run is shown in Figure 8. A comparison of this spectrum to those for both "light" and "heavy" 1,2,4- and 1,3,5-trichlorobenzenes (Figures 3, 4, 5, 6) indicates that all absorption bands can be assigned to these compounds except those at 2.78, 3.26, 3.43, and 3.55 microns. The latter are weak and are due to small quantities of methanol and methanol-d extracted along with the trihalobenzenes. Among the absorption bands found in the carbon disulfide extract of the product, the one at 8.430 microns is due to deuterio-1,2,4-trichlorobenzene.

Another possible explanation for the appearance of an absorption band at 8.430 microns is that some other reaction product, not containing deuterium, is formed in the dehydrohalogenation which happens to absorb at this wave length. This possibility was eliminated by carrying out a reaction in exactly the same manner as the one in methanol-d but using methanol as solvent. This spectrum is shown in Figure 7 and clearly indicates that this is not the case.

Since the extinction coefficients for the protium and deuterium compounds are known, a crude calculation of the hydrogen to deuterium ratio can be made using the optical densities obtained from Figure 8.

$$\frac{C_H}{C_D} = \frac{D_H \epsilon_D}{D_D \epsilon_H} = \frac{0.603 \times 33.73}{0.082 \times 167.2} = 1.48$$

Therefore, about 40 per cent of the 1,2,4-trichlorobenzene product contains deuterium. This estimate of the deuterium content of the 1,2,4-trichlorobenzene is believed to be reliable within 25 per cent; that is, the material contains 40 $\pm$ 10 per cent deuterio-1,2,4-trichlorobenzene. The infrared spectrum of a synthetic mixture containing 25 per

cent deuterio-1,2,4-trichlorobenzene and 75 per cent protio-1,2,4-trichlorobenzene is shown in Figure 9. There appears to be a greater hydrogen to deuterium ratio of the trichlorobenzene compounds in this mixture than in the product of the reaction between beta-benzene hexachloride and sodium methoxide in methanol-d (Figure 8).

CHAPTER IV

DISCUSSION AND CONCLUSIONS

The rate constants given in Table 1, Chapter III, indicate clearly that in the present work fluorine is more effective than chlorine in facilitating removal of deuterium from an aromatic nucleus. Thus, the reactivity order is

$$C_6H_3F_2D > C_6H_2Cl_3D > C_6H_3ClFD > C_6H_3Cl_2D$$

with the relative rates at 100° being 48.7: 12.1: 7.5: 1, respectively. The replacement of one chlorine on dichlorobenzene by fluorine increases the rate seven and one-half fold and the replacement of the second chlorine by fluorine increases the rate six and one-half fold. The limited number of compounds studied precludes our making broad generalizations concerning these effects but it does appear that changing the halogen to a more electronegative halogen or addition of a third halogen increases the rate of carbanion formation.

Hall, Piccolini, and Roberts (2) have investigated the deuterium exchange effect of fluoro, trifluoromethyl, methoxy, methyl, and hydrogen substituents on benzene. In liquid ammonia solutions using potassium amide as the base they found that fluorine and trifluoromethyl substituents (particularly those ortho to the deuterium) were able to facilitate deuterium exchange while the methoxy group was somewhat effective. Methyl and hydrogen were not very effective. These authors attribute the greater effectiveness of fluoro and trifluoromethyl groups

to inductive and field effects rathen than to electromeric effects which they considered minor. This explanation is reasonable in view of the fact that they almost invariably found the order

ortho > meta > para

in the effectiveness of the various groups to promote deuterium exchange. For example, the first order rate constants for deuterium exchange of ortho, meta, and para-deuterio fluorobenzene are 4×10^{-1}, 4×10^{-4} and 2×10^{-5} sec.$^{-1}$, respectively. In view of these facts, in all probability it is the hydrogen ortho to the two halogens in the compounds studied which undergoes exchange with the solvent.

Any explanation of the present results based on the electromeric effect would have fluorine expanding its outer energy level of electrons beyond the octet. This is thought to be energetically unfavorable (16).

According to Roberts and coworkers (18) both fluorobenzene and chlorobenzene form carbanions at measurable rates in liquid ammonia-potassium amide solutions. The chlorobenzene carbanion, but not the fluorobenzene carbanion, in this strongly basic solution tended to lose halide ions and form benzyne. By running the reactions in methanol in place of liquid ammonia, using lower base concentrations, and using compounds containing two halogens ortho to the hydrogen to activate it,simple deuterium-hydrogen exchange was observed without apparent side reactions involving benzyne formation.

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16. J. Hine, N. W. Burske, M. Hine, and P. B. Langford, J. Am. Chem. Soc., 79, 1406 (1957).

18. J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, J. Am. Chem. Soc., 78, 601 (1956).

Huisgen and coworkers (19) studied the rate of carbanion formation of some mono-and disubstituted benzenes. Substituents included fluoro, chloro, bromo, iodo, trifluoro, methyl, and methoxy. Their studies involved the reversible reaction between the aryl compound (for example ortho-dibromobenzene) and lithium piperidide to form the dihalo-organic lithium derivative. The latter subsequently decomposed to a benzyne. The first step was found to be rate controlling. The addition of a second bromine in the meta position to bromobenzene increased the rate of carbanion formation from 4.46×10^{-4} l./mole sec. to 1000×10^{-4} l./mole sec. Substitution of fluorine for one of these bromines increased the rate to $9,650 \times 10^{-4}$ l./mole sec. These data are not strictly comparable to the present ones, partly because of the more concentrated solutions used and partly because of the steric requirements of the piperidide ion, but they do show a somewhat similar general trend.

Since in the present case the reactions followed first-order kinetics well and since there are several other examples of such carbanion formation in the literature, it is probable that the observed reactions are indeed those of carbanion formation from the di- or trihalobenzene and methoxide ions.

There are two possible mechanisms for bimolecular eliminations of hydrogen and another group, such as halogen, from adjacent carbon atoms which fit a part of the observed experimental facts concerning these reactions (1, 20). Thus, in the elimination of HX from organic

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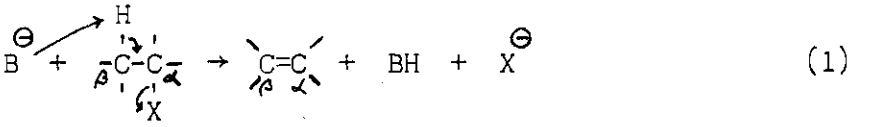
19. R. Huisgen, W. Mack, K. Herbig, N. Ott, and E. Anneser, Ber., 93, 412 (1960).

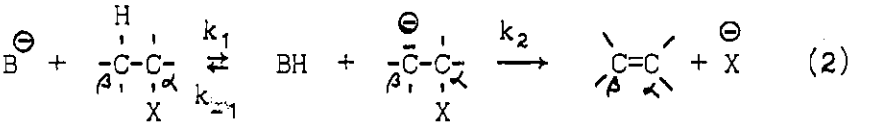
20. For a general discussion of elimination reactions see J. Hine, Physical Organic Chemistry, McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Ch. 7.

halogen compounds, a concerted mechanism where the electrons from the beta C-H bond are forming the double bond between the two carbons simultaneously with the removal of the halogen as a negative ion



(1)

or a stepwise mechanism involving a carbanion



(2)

are possible.

Although both mechanisms will follow second-order kinetics (first order in base, first-order in halide), there are two ways to determine which of the two mechanisms is followed. One can run the reaction in a deuterated solvent and inspect the unreacted halide for deuterium content. This will indicate whether or not the first step in Equation (2) is appreciably reversible. If C has more than one hydrogen or if there is more than one carbon which can lose a hydrogen, one can also inspect the product for deuterium content. Another way of obtaining such information is to examine the reaction for general base catalysis. In Equation (2), if k_2 is much larger than k_{-1}, the reaction velocity will be equal to $k_1[\text{halide}][B^-]$ and will exhibit general base catalysis. On the other hand, if k_{-1} is much larger than k_2, the reaction will exhibit specific base catalysis. Thus the observation of general base catalysis shows that no intermediate carbanion is being formed in equilibrium with the reactant. It does not, however, rule out the possibility of the formation of a carbanion that is usually transformed to product.

In utilizing deuterium exchange to investigate the mechanisms of elimination reactions, Skell and Hauser (21) studied the reaction of beta-phenylethyl bromide with sodium ethoxide in "heavy" ethanol. The unreacted bromide remaining after partial reaction contained no appreciable amount of deuterium and they concluded that a one-step elimination (E2) had occurred. It is to be noted that in this compound, a molecular conformation where the beta hydrogen and the alpha bromine atoms are trans to each other is easily possible. This facilitates the one-step mechanism (22). Hill and coworkers (5) investigated this same reaction and obtained similar results. They also found that 2-ethylbutyl bromide-2d, when allowed to react with potassium amide in liquid ammonia did not exchange deuterium for hydrogen.

Many halogen compounds containing beta hydrogen are known to exchange hydrogen for deuterium under relatively mild conditions. Miller and Noyes (23) found that trichloroethylene underwent extensive deuterium exchange under conditions milder than those required for elimination. Leitch and Bernstein (6) found that 1,1,2,2-tetrachloroethane when allowed to react with $Ca(OD)_2$ in D_2O gave trichloroethylene partly labeled with deuterium. The extent of exchange was estimated by Cristol (7) from the data of Leitch and Bernstein to be 10 to 15 per cent.

Hine, Wiesboeck, and Ghirardelli (24) investigated the deuterium exchange of deuterio-2,2-dihalo-1,1,1-trifluoroethanes. No appreciable

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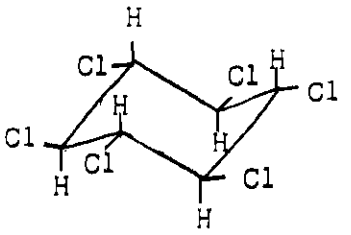
21. P. S. Skell and C. R. Hauser, J. Am. Chem. Soc., 67, 1661 (1945).
22. C. K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, Ithaca, N. Y., 1953, p. 467.
23. S. I. Miller and R. M. Noyes, Jr., J. Am. Chem. Soc., 74, 636 (1952).
24. J. Hine, R. Wiesboeck, and R. G. Ghirardelli, J. Am. Chem. Soc., 83, 1219 (1961).

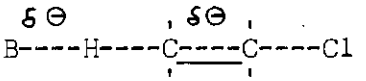
side reactions occurred and the following order of effectiveness in facilitating deuterium exchange by halogens was observed

$$Br > I > Cl$$

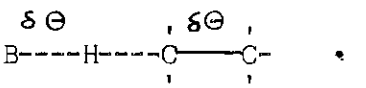
Cristol (1) studied the alkaline dehydrohalogenation of benzene hexachlorides and found that the beta isomer, in which all the chlorines and trans to each other,



reacts much more slowly than the alpha, gamma, and delta isomers, which have at least one trans HCl pair. He indicated that the beta isomer reacts first by forming a carbanion which subsequently decomposes to give a product that rapidly loses two more moles of hydrogen chloride. Cristol, Hause, and Meek (4) discuss the reasons why the cis arrangement has a relatively low activity. Steric repulsions and repulsion of the negative base ion by the cis chlorine are said to be minor effects. The major effect is said to be due to the fact that between 7 and 14 kcal. less activation energy are required to produce the transition state for the concerted trans elimination



than for producing the transition state of the first step in the cis elimination



The activation energy they determined, which is about 10 kcal. higher for the beta compound, tends to substantiate this.

Cristol and Fix (7) tested the possibility of carbanion formation by dehydrohalogenating beta benzene hexachloride with sodium ethoxide in "heavy" ethanol. After 50 per cent reaction, the unreacted halide isolated was found to contain deuterium in about 0.08 per cent of the molecules. From this data they assumed the formation of a carbanion of the halide which reacted with the solvent to give deuterio-beta-benzene hexachloride.

Carbanion formation can be observed in systems where trans eliminations are sterically possible if the acidity of the beta hydrogen is sufficiently high. For example, Hine and Kaplan (25) found that the basic decomposition of 1,1,1,3-tetranitro-2-phenylpropane to nitroform and beta-nitrostyrene is subject to general base catalysis and that the rate-controlling step in acid solution is the decomposition of the carbanion formed by loss of one of the hydrogens on carbon three. Their conclusion is that in acid solution the ElcB mechanism is operating.

In investigating the rates of dehydrohalogenation of 2,2-dihalo-1,1,1-trifluoroethanes, Hine, Wiesboeck, and Ramsay (26) found a carbanion mechanism, undoubtedly due to the activation of the hydrogen by the two halogens (I, Br, or Cl) and the strongly electron-withdrawing trifluoromethyl group on the same carbon. This explanation seems especially reasonable here because the fluorine on the carbon adjacent

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25. J. Hine and L. A. Kaplan, J. Am. Chem. Soc., 82, 2915 (1960).
26. J. Hine, R. Wiesboeck, and O. B. Ramsay, J. Am. Chem. Soc., 83, 1222 (1961).

to the hydrogen is difficult to remove[1] and the system would form a relatively stable carbanion.

Also, Bordwell and Kern (27) found the second-order reaction between hydroxide ions and trans-2-(p-tolylsulfonyl)-cyclohexyl p-toluenesulfonate gave 1-p-tolylsulfonyl-1-cyclohexene rather than 3-p-tolylsulfonyl-1-cyclohexene. This preference for cis elimination then is due to the activation of the hydrogen by the p-tolylsulfonyl group attached to the same carbon and to the p-tolylsulfoxyl group attached to the adjacent carbon. These authors speculate that $-NO_2$, -CN, -COR, and $-CO_2R$ groups also can activate the hydrogen enough to cause cis elimination. Weinstock, Pearson, and Bordwell (28) in discussing these results state that if the hydrogen-carbon bond is sufficiently weak and the bond between carbon and the leaving group sufficiently strong, the ElcB mechanism will operate. However, they conclude that the above reactions are E2 because general base catalysis was observed.

In a reaction very closely related to the present work on beta benzene hexachloride, Goering, Relyes, and Howe (29) found that electron withdrawing groups in the para position in either cis- or trans-2-chlorocyclohexyl phenyl sulfone

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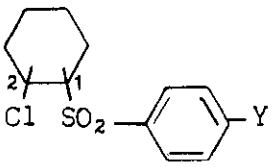
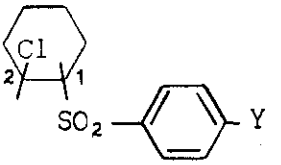
[1] One of the products was found to be fluoride ions.

27. F. G. Bordwell and R. J. Kern, J. Am. Chem. Soc., 77, 1141 (1955).

28. J. Weinstock, R. G. Pearson, and F. G. Bordwell, J. Am. Chem. Soc., 78, 3473 (1956).

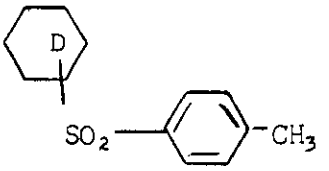
29. H. L. Goering, D. I. Relyea, and K. L. Howe, J. Am. Chem. Soc., 79, 2502 (1957).





increase the rate of dehydrochlorination. Both are said to undergo a cis elimination by a two step process involving abstraction of the C_1 hydrogen followed by conversion of the anion to the elimination product. The first step, carbanion formation, is rate controlling and irreversible in 80 per cent ethanol at hydroxide ion concentrations of 0.004 to 0.03 M. The trans compound is very similar to beta-benzene hexachloride, the C_1 hydrogen is activated sufficiently by the electron withdrawing groups to cause carbanion formation.

Weinstock, Bernardi, and Pearson (30) studied the deuterium exchange of cyclohexyl-1-d p-tolyl sulfone



and found the deuterium exchange rate to be 10^3 to 10^5 times slower than the cis elimination rate of the corresponding tosylate compounds which they had previously studied. This does not eliminate the carbanion mechanism, though, because in the tosylate compounds there is the added inductive

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30. J. Weinstock, J. L. Bernardi, and R. G. Pearson, J. Am. Chem. Soc., 80, 4961 (1958).

effect of the tosylate group which would certainly make the deuterium more acidic. Their crude estimates indicate that the tosylate compounds they studied could not exchange hydrogen more than 1/100 as fast as the elimination reaction. This would tend to rule out the carbanion mechanism for these compounds. However, Hine and Ramsay (31) have found that a 2-methoxy substituent increases the rate of deuterium exchange of cyclohexyl p-tolyl sulfone by a factor of 500, a considerably larger factor than that estimated by Weinstock, Bernardi, and Pearson (30) for the much more strongly electron withdrawing tosylate substituent. Hine and Ramsay use the Taft equation to estimate the rate which would be expected for the deuterium exchange of the tosylate compound and found that the rate of cis elimination is slower than would be predicted for carbanion formation. Possibly the large tosylate group is responsible for this retarding effect.

From the above discussion, it can be concluded that the "deuterium exchange test" and the "kinetic test" for the ElcB mechanism will not necessarily, in every case, tell if this mechanism is in operation. For example, if the carbanion formed almost invariably decomposes to product rather than reacting with solvent, neither test will indicate this mechanism. The carbanion mechanism, though, can be observed in cases where the hydrogen is easily lost and the other group is difficultly lost.

It is believed that the present observation, that the 1,2,4-trichlorobenzene produced from the dehydrochlorination of beta-benzene hexachloride in methanol-d contains deuterium,gives added light on the mechanism of

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31. J. Hine and O. B. Ramsay, J. Am. Chem. Soc., 84, 973 (1962).

this elimination reaction. First, however, it is of importance to learn whether the deuterium was already in the 1,2,4-trichlorobenzene when it was formed or whether it got there after the trichlorobenzene was formed, via a base-catalysed exchange with the solvent. In view of the fact that the rate constant for the deuterium exchange of 3-deuterio-1,2,4-trichlorobenzene with light methanol in the presence of a sodium methoxide catalyst is only about one-hundredth as large as the second order rate constant for the dehydrohalogenation of beta-benzene hexachloride, it does not seem likely that very much of the deuterium found in the trichlorobenzene could have gotten there by subsequent exchange of an initially undeuterated product. Nevertheless, an estimate of the maximum amount of deuterium that could have been picked up by such exchange will be made. The rate-controlling step in the exchange reaction would be the removal of a proton from the 3-position of 1,2,4-trichlorobenzene by a methoxide ion. This would be faster than the removal of the deuteron from 3-deuterio-1,2,3-trichlorobenzene, a reaction whose rate constant has been found to be 2.44×10^{-4} l./mole sec. in methanol at 100°, because of a kinetic isotope effect. It seems unlikely that this deuterium kinetic isotope effect (k_H/k_D) will be larger than about 5.5, a "full" isotope effect at 100°, corresponding to a k_H/k_D of 8.3 at 25° (32), and it may be much smaller. Therefore, the rate constant for removal of a proton from the trichlorobenzene by methoxide ions in methanol at 100° should be no larger than 13.4×10^{-4}

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32. L. Melander, Isotope Effects on Reaction Rates, Ronald Press Co., New York, N. Y., 1960, pp. 20-22.

l./mole sec. Since it is desired to estimate the rate constant in methanol-d, the possibility of a solvent isotope effect must be considered. In several cases deuteroxide ions in heavy water have been found to remove protons from carbon 20 to 45 per cent faster than hydroxide ions in light water (33, 34, 35, 36). This is a case in which there is an isotopic change in the nature of the base as well as in that of the solvent. Long and Watson (37) have found acetate ions to remove protons from methylacetylacetone 30 per cent faster in light water than in heavy water. In any event, since a change in the isotopic nature of one-sixth of the atoms in methanol should have a smaller effect than a change in the isotopic nature of two-thirds of the atoms in water, solvent deuterium isotope effects would not be expected to be so strong in methanol as in water. Therefore, it seems unlikely that the rate constant for the removal of the deuteron from 3-deuterio-1,2,4-trichlorobenzene by methoxide ion in methanol-d will be more than 13.4×10^{-4} l./mole sec.

Assuming that the rate constant for the dehydrohalogenation of beta-benzene hexachloride is the same in methanol-d as in light methanol, the concentrations of sodium methoxide and of 1,2,4-trichlorobenzene can be calculated at various times for the experiment in which benzene hexachloride was dehydrochlorinated in methanol-d. Then by using the average concentration of the reactants over various 100 sec. time intervals and multiplying by the time and the estimated maximum possible rate constant

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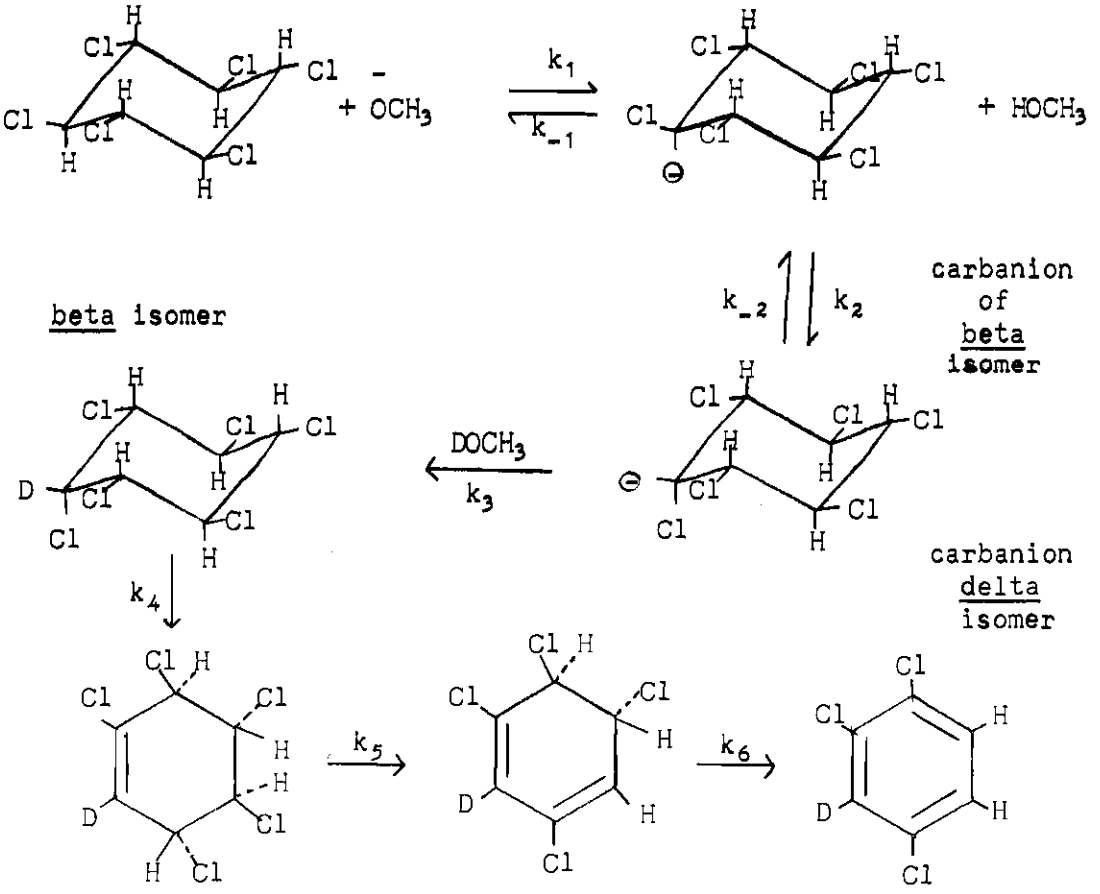
33. W. E. Nelson and J. A. V. Butler, J. Chem. Soc., 957 (1938).
34. S. H. Maron and V. K. La Mer, J. Am. Chem. Soc., 60, 2588 (1938).
35. O. Reitz, Z. physik, Chem., A183, 371 (1939).
36. O. Reitz, ibid., A177, 85 (1936).
37. F. A. Long and D. Watson, J. Chem. Soc., 2019 (1958).

it can be shown that not more than 10.7 per cent deuteration of the trichlorobenzene could have occurred after the trichlorobenzene was formed (see the Appendix for this calculation). Hence most of the 40 ± 10 per cent deuterium found must have already been in the 1,2,4-trichlorobenzene when it was formed.

In view of Cristol and Fix's observation that there is deuterium exchange with the beta-benzene hexachloride (7) and the present observation that there is deuterium in the 1,2,4-trichlorobenzene formed, the following reaction mechanism seems plausible.



The presence of deuterium in the trichlorobenzene can be explained by assuming that the carbanion of the beta isomer of benzene hexachloride inverts to give the carbanion of the delta isomer which abstracts deuterium from the solvent. This compound has H and Cl atoms trans to each other and elimination can occur removing these atoms but leaving the deuterium attached to the double bonded carbon in the cyclohexene intermediate. If two cis eliminations occur from this intermediate, the product will be a deuterio-trichlorobenzene.

APPENDIX

TABLES

Method of Estimation of the Extent of Hydrogen-Deuterium Exchange by the Trichlorobenzene Product During the Dehydrochlorination of beta-Benzene Hexachloride in Methanol-d.

In the dehydrochlorination of beta-benzene hexachloride in methanol-d, it was found after about 95 per cent reaction that 40 ± 10 per cent of the 1,2,4-trichlorobenzene product contained deuterium (see p. 50). Since the rate constant for the dehydrohalogenation reaction and that for the deuterium-hydrogen exchange reaction of 1,2,4-trichlorobenzene are known, it is possible to estimate whether the deuterium in the product got there by methoxide-catalysed exchange with the solvent after the product was formed or whether it was there due to a methoxide-catalysed reaction between solvent and the starting beta-benzene hexachloride.

During the time of the reaction (25 minutes at 100°) the beta-benzene hexachloride and sodium methoxide concentrations continuously decreased while the 1,2,4-trichlorobenzene concentration continuously increased. Thus, we are dealing with consecutive second order reactions. The kinetic equation for the dehydrochlorination reaction (see p.59) is

$$k_2 t = \frac{2.303}{(b - 3a)} \log \frac{a\,(b - 3x)}{b\,(a - x)}$$

where a and b are the initial halide and base concentrations, respectively. We shall let x be the change in halide concentration at time t. In this particular reaction a = 0.01849 mole /liter and b = 0.1185 mole/liter.

The k_2 value for this reaction is 239 x 10^{-4} l./mole sec. By substituting the value for a, b, and k_2 into the above equation and rearranging we get

$$\log \frac{b - 3x}{a - x} = 6.98 \times 10^{-4} t + 0.8068$$

By choosing small time intervals of 100 sec. and using the estimated average benzene hexachloride and methoxide concentrations and using the maximum estimated rate constant for hydrogen-deuterium exchange in the 1,2,4-trichlorobenzene of 13.4 x 10^{-4} l./mole sec., the total concentration of deuterio-1,2,4-trichlorobenzene can be calculated by using the equation

$$\frac{\Delta x}{\Delta t} = k_2 [C_6H_3Cl_3][NaOCH_3]$$

The values are shown in the following table.

t,sec.	$\log \frac{(b - 3x)}{(a - x)}$	x	b - 3x	$\Delta x \times 10^4$
0	0.8068	0.0000	0.1185	
100	0.8766	0.0046	0.1047	0.35
200	0.9464	0.0078	0.0951	0.83
300	1.0162	0.0100	0.0885	1.08
400	1.0860	0.0117	0.0834	1.23
500	1.1558	0.0130	0.0795	1.31
600	1.2256	0.0140	0.0765	1.36
700	1.2954	0.0147	0.0744	1.38
800	1.3652	0.0154	0.0723	1.39
900	1.4350	0.0159	0.0708	1.41
1000	1.5048	0.0165	0.0696	1.42
1200	1.6444	0.0170	0.0675	2.83
1500	1.8538	0.0176	0.0657	4.18
			Total	18.77

A total maximum of 0.001877 moles per liter of trichlorobenzene product would have exchanged by the time the reaction was terminated. However, since the starting concentration of benzene hexachloride was 0.01849 mole/liter and the reaction went to 95 per cent completion, 0.0176 mole/liter of trichlorobenzene product had been formed. Therefore, the per cent deuteration by exchange is 0.00188 x 100/0.176 or 10.7 per cent. It seems then that only about one-fourth of the deuterio-1,2,4-trichlorobenzene found in the product was formed by exchange and this value is a maximum one because a maximum value for the estimated rate of hydrogen-deuterium exchange was used.

Table 1. Kinetic Constants for Deuterium Exchange and Dehydrohalogenation in Methanol.

Compound	$10^6 k_2$(a) 50.0°	70.0°	100°	120°	$\triangle H^{\ddagger}$, k.cal./mole	$\triangle S^{\ddagger}$, e.u.
$C_6H_3F_2D$	2.88 ± 0.04		978.0 ± 35.3		27.3 ± 0.2	-4.3 ± 0.7
C_6H_3ClFD		4.47 ± 0.13	151.0 ± 2.8		29.2 ± 0.5	-2.9 ± 1.4
$C_6H_3Cl_2D$			20.2 ± 0.77	153.0 ± 6.4	28.6 ± 1.0	-8.6 ± 2.8
$C_6H_2Cl_3D$		4.78 ± 0.23	244.0 ± 5.8		32.8 ± 0.5	7.6 ± 1.5
$-C_6H_6Cl_6$(b)		3.29 ± 6.4	23,900 ± 740		35.7 ± 0.1	29.3 ± 0.4

(a) l./mole sec.

(b) Dehydrohalogenation in Methanol, l./mole sec.

Table 2. $C_6H_3F_2D$ + CH_3ONa in CH_3OH at 50.0°C.

$(C_6H_3F_2D)_o$ = 0.009891 M — 10 ml. samples

$(CH_3ONa)_o$ = 0.09676 M — % D = 67.4

ϵ_H = 243.7 — ϵ_D = 587.6

Times in Hours	Optical Densities: H Compound	Optical Densities: D Compound	C_H/C_D	$\log [p_o + p_o(C_H/C_D)]$
209.25	0.116	0.344	0.815	0.08743
307.37	0.068	0.161	1.020	0.1339
384.58	0.095	0.194	1.181	0.1670
477.45	0.158	0.270	1.413	0.2106
620.58	0.238	0.388	1.479	0.2232

k_1 (from plot) = $(1.00 \pm 0.013) \times 10^{-3}$ hr.$^{-1}$

k_1 = $(2.79 \pm 0.04) \times 10^{-7}$ sec.$^{-1}$

k_2 = $(28.8 \pm 0.4) \times 10^{-7}$ l./mole sec.

Table 3. $C_6H_3F_2D$ + CH_3ONa in CH_3OH at 100°C.

$(C_6H_3F_2D)_o$ = 0.009139 M — 10 ml. samples

$(CH_3ONa)_o$ = 0.09030 M — % D = 67.4

ϵ_H = 243.7 — ϵ_D = 587.6

Times in Hours	Optical Densities		C_H/C_D	$\log[p_o + p_o(C_H/C_D)]$
	H Compound	D Compound		
0.9166	0.162	0.369	1.058	0.1421
1.642	0.192	0.326	1.419	0.2122
2.193	0.213	0.277	1.855	0.2842
2.905	0.229	0.190	2.907	0.4205
5.200	0.098	0.037	6.385	0.6970

k_1 (from plot) = $(3.18 \pm 0.12) \times 10^{-1}$ hr.$^{-1}$

k_1 = $(883 \pm 32) \times 10^{-7}$ sec.$^{-1}$

k_2 = $(9780 \pm 353) \times 10^{-7}$ l./m. sec.

Table 4. C_6H_3ClFD + CH_3ONa in CH_3OH at 70.0°C

$(C_6H_3ClFD)_o$ = 0.008883 M — 10 ml. samples

$(CH_3ONa)_o$ = 0.09435 M — % D = 74.0

ϵ_H = 129.7 — ϵ_D = 339.6

Times in Hours	H Compound	D Compound	C_H/C_D	$\log[p_o + p_o(C_H/C_D)]$
22.35	0.070	0.452	0.4055	0.0170
160.60	0.116	0.409	0.7425	0.1106
353.60	0.167	0.325	1.345	0.2394
569.30	0.210	0.242	2.272	0.3840
832.60	0.234	0.166	3.691	0.5405
1075.20	0.124	0.065	5.000	0.6479

k_1 (from plot) = $(1.52 \pm 0.043) \times 10^{-3}$ hr.$^{-1}$

k_1 = $(4.22 \pm 0.12) \times 10^{-7}$ sec.$^{-1}$

k_2 = $(44.7 \pm 1.3) \times 10^{-7}$ l./m. sec.

Table 5. C_6H_3ClFD + CH_3ONa in CH_3OH at 100°C.

$(C_6H_3ClFD)_0$ = 0.008502 M — 10 ml. samples

$(CH_3ONa)_0$ = 0.09030 M — % D = 74.0

ϵ_H = 129.7 — ϵ_D = 339.6

Times in Hours	Optical Densities		C_H/C_D	$\log[p_0 + p_0(C_H/C_D)]$
	H Compound	D Compound		
3.0678	0.092	0.444	0.542	0.0577
6.100	0.120	0.379	0.828	0.1313
9.450	0.128	0.285	1.176	0.2068
13.200	0.152	0.249	1.598	0.2840
16.970	0.074	0.090	2.153	0.3675
20.570	0.131	0.129	2.659	0.4325

k_1 (from plot) = $(48.9 \pm 0.89) \times 10^{-3}$ hr.$^{-1}$

k_1 = $(136 \pm 2.5) \times 10^{-7}$ sec.$^{-1}$

k_2 = $(1510 \pm 28) \times 10^{-7}$ l./m. sec.

Table 6. $C_6H_3Cl_2D + CH_3ONa$ in CH_3OH at 100°C.

$(C_6H_3Cl_2D)_0 = 0.01594$ M — 10 ml. samples

$(CH_3ONa)_0 = 0.08976$ M — % D=67.25

$\epsilon_H = 126.9$ — $\epsilon_D = 304.7$

Time in Hours	Optical Densities		C_H/C_D	$\log[p_0 + p_0(C_H/C_D)]$
	H Compound	D Compound		
17.200	0.071	0.227	0.7508	0.07093
47.983	0.071	0.150	1.136	0.1573
68.783	0.073	0.120	1.460	0.2186
95.633	0.093	0.133	1.679	0.2557
140.55	0.110	0.112	2.359	0.3539

k_1 (from plot) $= (6.52 \pm 0.26) \times 10^{-3}$ hr.$^{-1}$

$k_1 = (18.1 \pm 0.72) \times 10^{-7}$ sec.$^{-1}$

$k_2 = (202 \pm 7.7) \times 10^{-7}$ l./m. sec.

Table 7. $C_6H_3Cl_2D + CH_3ONa$ in CH_3OH at 120°C.

$(C_6H_3Cl_2D)_0 = 0.01541$ M — 10 ml. samples

$(CH_3ONa)_0 = 0.08675$ M — % D = 67.25

$\epsilon_H = 126.9$ — $\epsilon_D = 304.7$

Time in Hours	Optical Densities		C_H/C_D	$\log[p_0 + p_0(C_H/C_D)]$
	H Compound	D Compound		
3.700	0.056	0.184	0.7306	0.06588
8.700	0.076	0.135	1.295	0.1885
13.03	0.132	0.138	2.300	0.3460
13.117	0.107	0.124	2.071	0.3148
18.15	0.108	0.113	2.295	0.3456
20.917	0.100	0.102	2.355	0.3533

k_1 (from plot) $= (47.8 \pm 2.0) \times 10^{-3}$ hr.$^{-1}$

$k_1 = (133 \pm 5.6) \times 10^{-7}$ sec.$^{-1}$

$k_2 = (1530 \pm 64) \times 10^{-7}$ l./m. sec.

Table 8. $C_6H_2Cl_3D + CH_3ONa$ in CH_3OH at 70.0°C.

$(C_6H_2Cl_3D)_0 = 0.01514$ M — 10 ml. samples

$(CH_3ONa)_0 = 0.09379$ M — % D = 87.06

$G_H = 167.2$ — $G_D = 33.73$

Time in Hours	Optical Densities: H Compound	Optical Densities: D Compound	C_H/C_D	$\log[p_0 + p_0(C_H/C_D)]$
97.000	0.082	0.047	0.3520	0.07082
167.37	0.260	0.110	0.4769	0.1192
190.65	0.569	0.180	0.6375	0.1540
311.55	0.585	0.148	0.7972	0.1944

k_1 (from plot) = $(1.61 \pm 0.08) \times 10^{-3}$ hr.$^{-1}$

k_1 = $(4.48 \pm 0.22) \times 10^{-7}$ sec.$^{-1}$

k_2 = $(47.8 \pm 2.3) \times 10^{-7}$ l./m. sec.

Table 9. $C_6H_2Cl_3D + CH_3ONa$ in CH_3OH at 100°C.

$(C_6H_2Cl_3D)_0 = 0.01449$ M — 10 ml. samples

$(CH_3ONa)_0 = 0.08976$ M — % D = 87.06

$\epsilon_H = 167.2$ — $\epsilon_D = 33.73$

Time in Hours	Optical Densities		C_H/C_D	$\log[p_0 + p_0(C_H/C_D)]$
	H Compound	D Compound		
1.200	0.345	0.253	0.2751	0.04530
2.400	0.344	0.175	0.3964	0.08483
3.833	0.540	0.204	0.5339	0.1256
4.950	0.330	0.090	0.7395	0.1802
6.883	0.413	0.089	0.9362	0.2268

k_1 (from plot) = $(7.90 \pm 0.19) \times 10^{-2}$ hr.$^{-1}$

k_1 = $(219 \pm 5.2) \times 10^{-7}$ sec.$^{-1}$

k_2 = $(2440 \pm 58) \times 10^{-7}$ l./m. sec.

Table 10. beta-Benzene Hexachloride + CH_3ONa in CH_3OH at 70.0°C.

$(\underline{beta}\text{-B.H.C.})_o$ = 0.01718 M 5.50 ml. samples

$(CH_3ONa)_o$ = 0.08545 M HCl 0.07582 M

Time in Hours	ml.HCl	$\log \frac{3a\ (b - 3x)}{b\ (3a - 3x)}$
1.925	5.82	0.03607
3.950	5.22	0.07805
6.133	4.77	0.1204
7.850	4.50	0.1364
10.117	4.23	0.1920
12.908	3.99	0.2354

k_2 (from plot) = 1.183 ± 0.023 l./m. hr.

k_2 = (3.286 ± 0.064) x 10^{-7} l./m. hr.

Table 11. *beta*-Benzene Hexachloride + CH_3ONa in CH_3OH at 100°C

($\underline{beta}$-B.H.C.)$_0$ = 0.01644 M — 5.50 ml. samples

$(CH_3ONa)_0$ = 0.08179 M — HCl = 0.07582 M

Time in Seconds	ml. HCl	$\log \frac{3a\ (b - 3x)}{b\ (3a - 3x)}$
178	5.33	0.06934
344	4.73	0.1247
680	3.85	0.2499
940	3.55	0.3418
1188	3.35	0.3845
1610	3.00	0.5982

k_2 (from plot) = 239,100 $\pm$ 7,400 x 10^{-7} l./m. sec.

Table 12. Extinction Coefficients for Aromatic Halides

Compound	Extinction Coefficient l./cm.mole	Wavelength in Microns
$C_6H_3F_2D$	587.6	9.812
$C_6H_3F_2H$	243.7	11.755
C_6H_3ClFD	339.6	10.933
C_6H_3ClFH	129.7	8.165
$C_6H_3Cl_2D$	304.7	13.484
$C_6H_3Cl_2H$	126.9	10.001
$C_6H_2Cl_3D$	33.73	8.430
$C_6H_2Cl_3H$	167.2	9.135

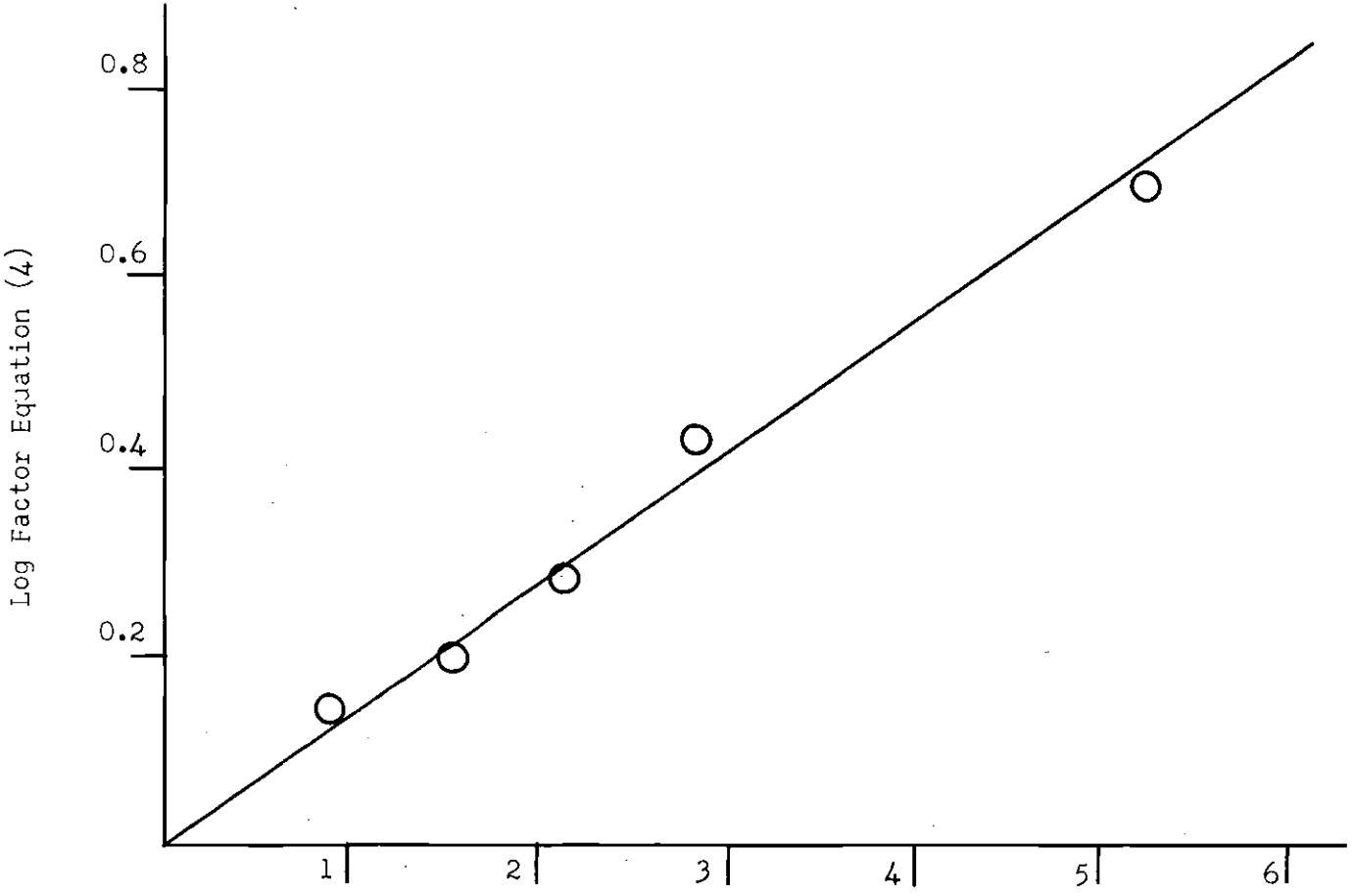


Figure 1. Log Factor of Equation (4) versus Time for Deuterium Exchange of $C_6H_3F_2D$ in CH_3OH at 100°C.

Slope = 7.25, $k = (3.18 \pm 0.12) \times 10^{-1}$ hr.$^{-1}$

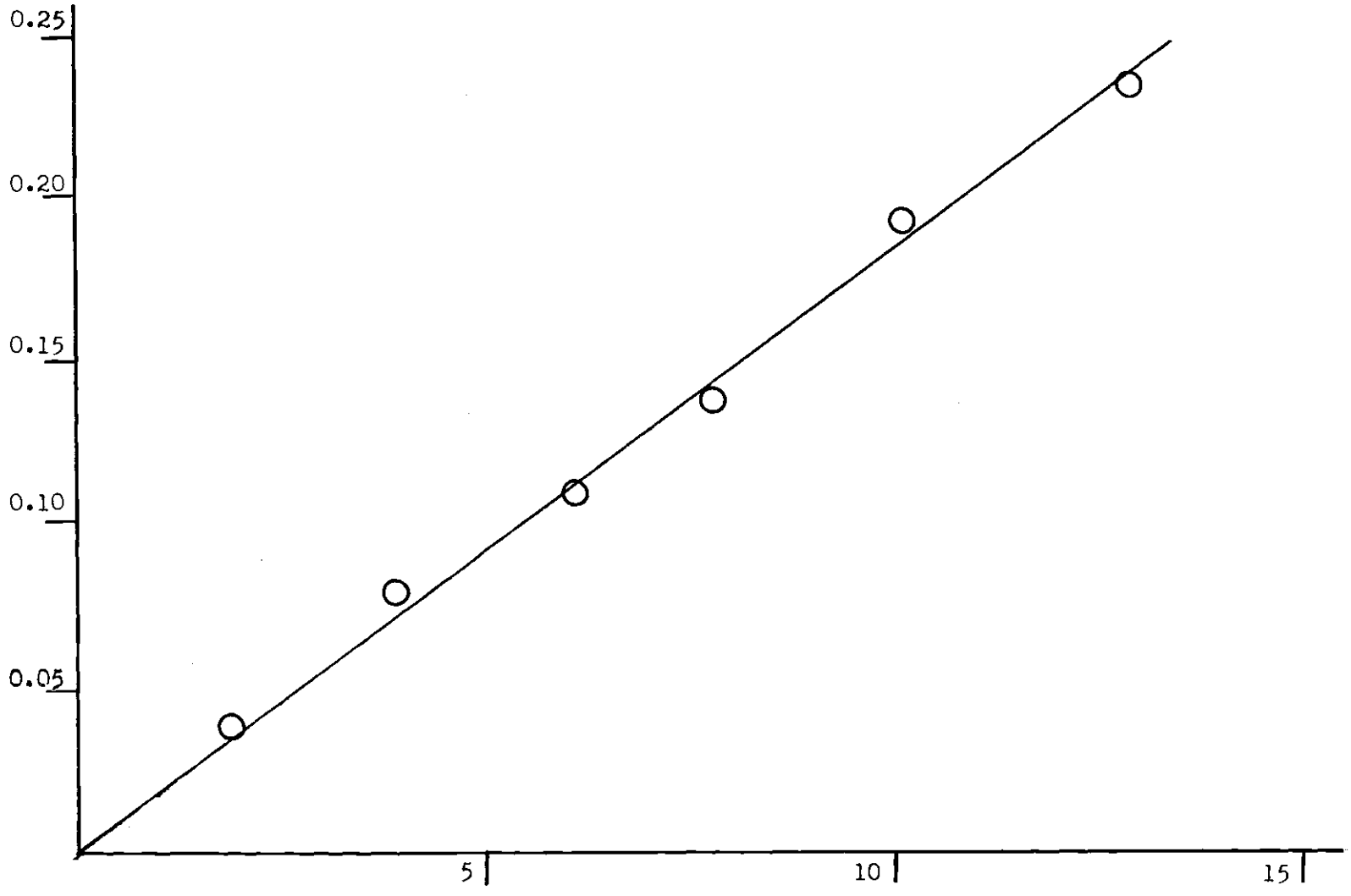


Figure 2. Dehydrohalogenation of beta-Benzenehexachloride at 70.0°C in Methanol

Slope = 54.5 ± 0.73 k_2 = 1.18 ± 0.023 l./m. hr.

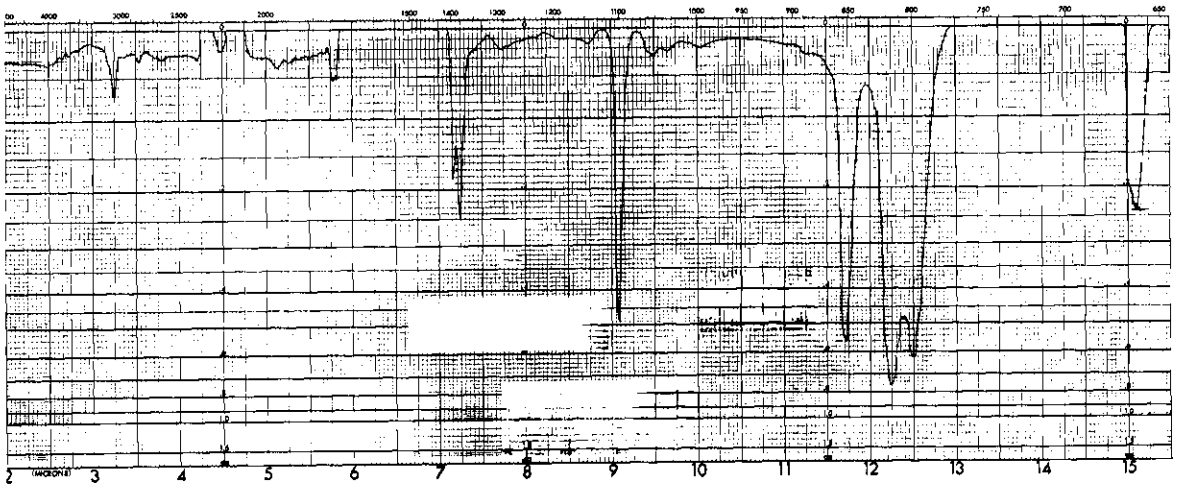


Figure 3. The Infrared Spectrum of 1,3,5-Trichlorobenzene.

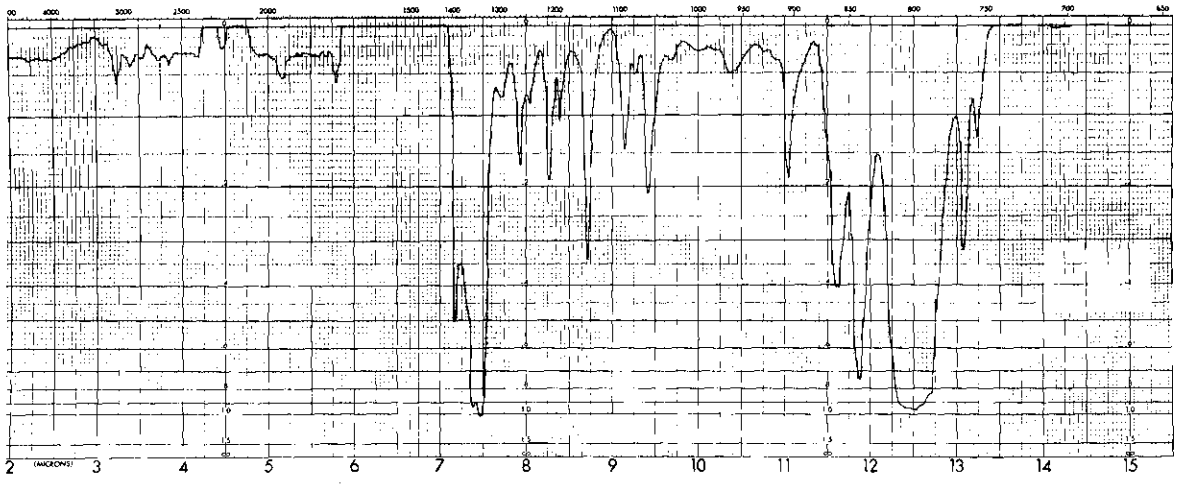


Figure 4. The Infrared Spectrum of Deuterio-1,3,5-Trichlorobenzene.

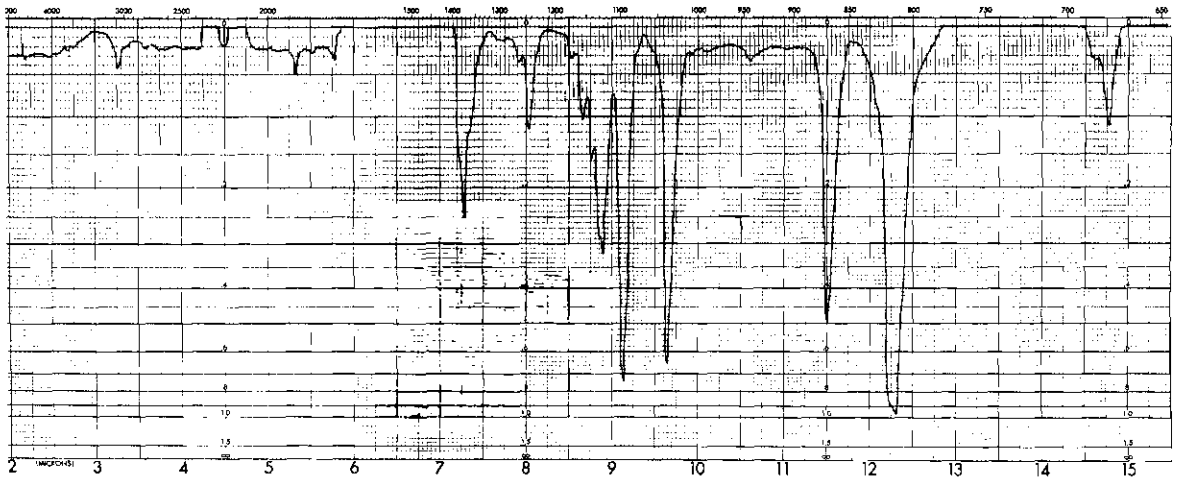


Figure 5. The Infrared Spectrum of 1,2,4-Trichlorobenzene.

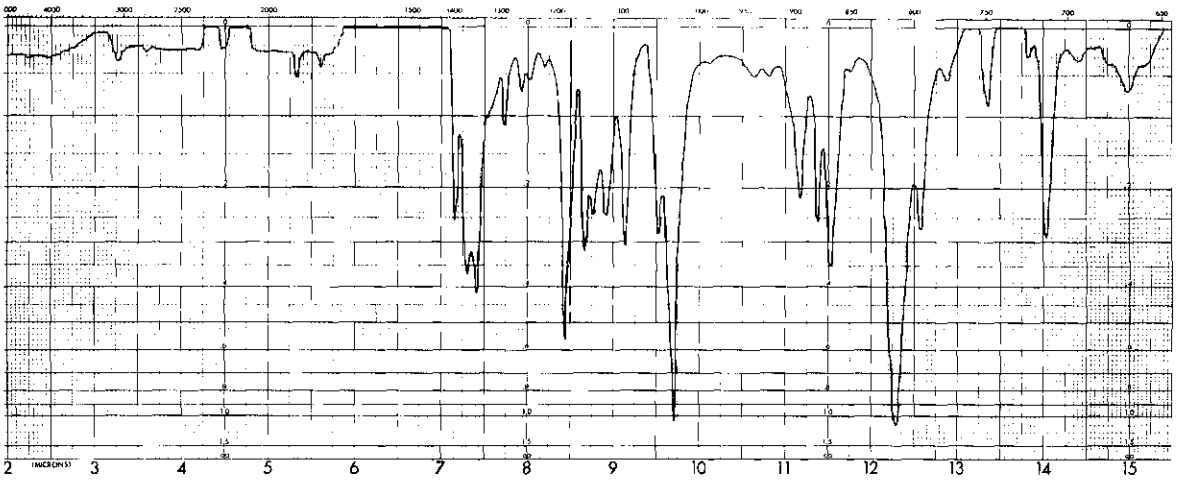


Figure 6. The Infrared Spectrum of Deuterio-1,2,4-Trichlorobenzene.

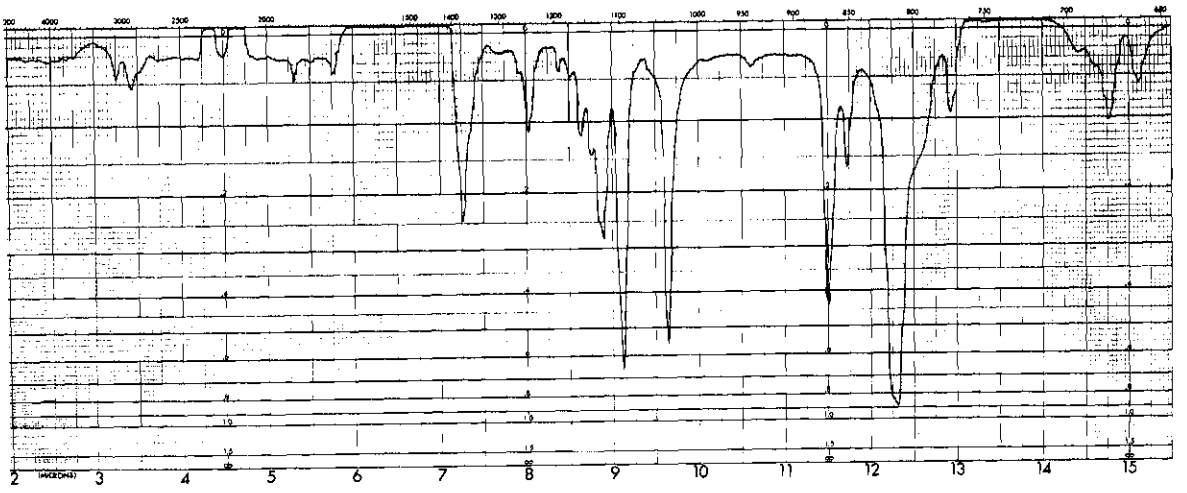


Figure 7. The Infrared Spectrum of the Reaction Product of <u>beta</u>-Benzene Hexachloride + CH_3ONa in CH_3OH at 100°C.

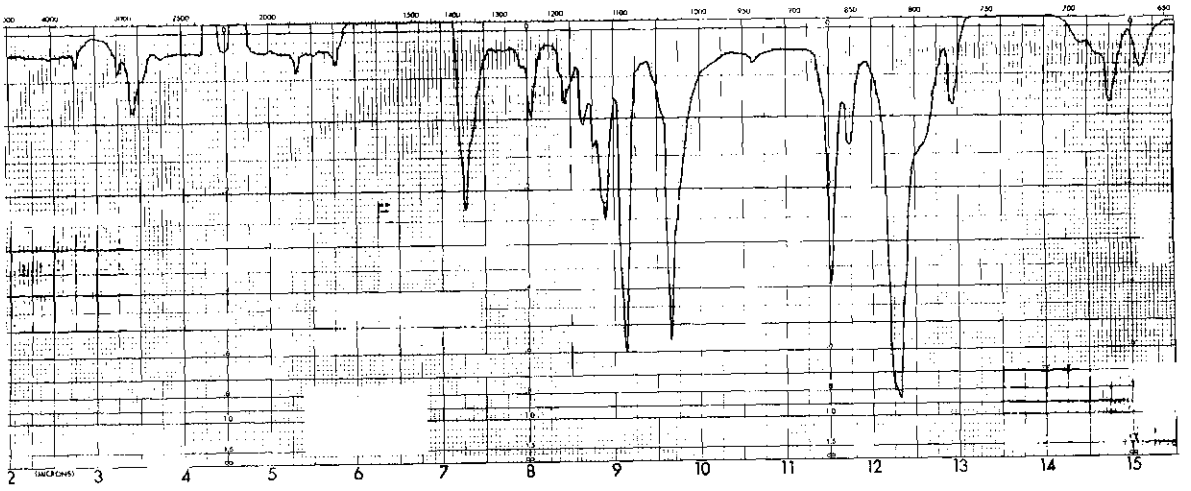


Figure 8. The Infrared Spectrum of the Reaction Product of <u>beta</u>-Benzene Hexachloride + CH_3ONa in CH_3OD at 100°C.

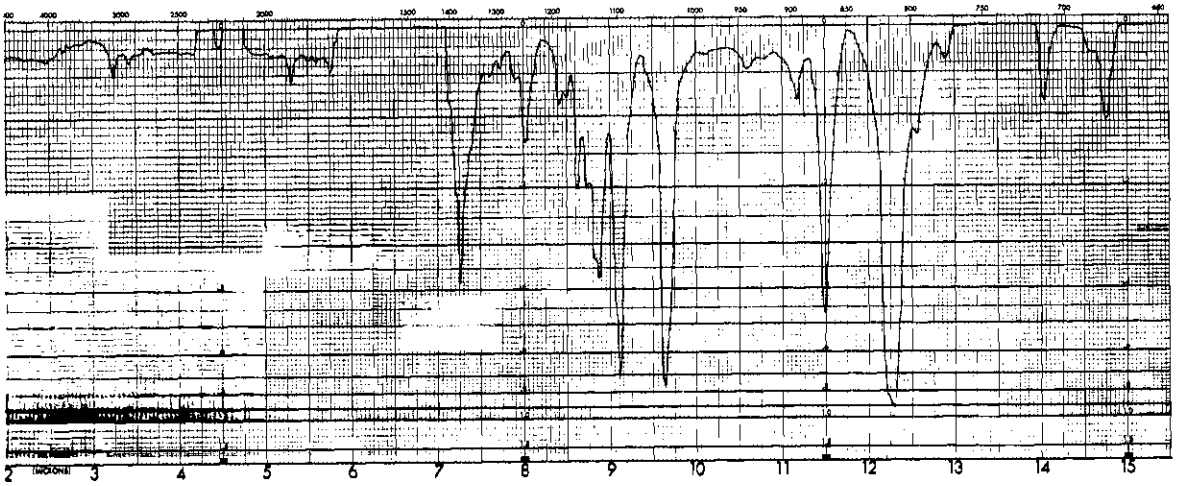


Figure 9. The Infrared Spectrum of a Mixture of Three Parts 1,2,4-Trichlorobenzene and the One Part Deuterio-1,2,4-Trichlorobenzene.

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VITA

Paul Brooks Langford was born on August 11, 1930 in Lockesburg, Arkansas, the son of Bernie (nee Potts) and John Brooks Langford. He attended primary and secondary schools in Lockesburg and graduated from high school in May, 1948. He entered Southern State College in Magnolia, Arkansas in September, 1948 and after two years transferred to Oklahoma State University in Stillwater, Oklahoma where he received the Bachelor of Science degree in Chemistry in June, 1952. After teaching and doing research there for two years he received the Master of Science degree in Chemistry in August, 1954. He entered Georgia Institute of Technology the same year and held research fellowships from the National Science Foundation and Instructorships in the School of Chemistry which supported his work until June, 1962. In June, 1959 he was married to Beverly Joyce Arnau of Atlanta. He has accepted a position as Assistant Professor of Chemistry at David Lipscomb College in Nashville, Tennessee.